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The Problem of Proportioning Portland
Cement Raw Mixtures

Part I —A General View of the Problem

Part II —Mathematical Study of the Problem

Part III—Application to Typical Processes

Part IV—Direct Control of Potential Composition

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The Problem of Proportioning Portland Cement Raw Mixtures

Part I — A General View of the Problem

By L. A. DAHL*

This series of articles on raw mixture control will cover mathematical studies, application to typical processes, and direct control of potential composition

PORTLAND CEMENT CLINKER is manufactured by heating a finely ground mixture of calcareous and argillaceous materials in a kiln at a temperature of partial fusion. This process is generally referred to as "burning." The mixture of raw materials is the *raw mix*. There is a considerable variety of materials which may be used. For example, the calcareous material may be limestone, oyster shells or marl. The argillaceous material may be shale or clay. In some districts cement rock is used. This rock contains both calcareous and argillaceous constituents in varying proportions, but in approximately the proportions required in the raw mix. The principles involved in proportioning the raw materials are the same for these various materials. It will therefore be sufficient to refer to the materials as limestone and shale, with the understanding that the principles and methods discussed are applicable to any of the raw materials in common use.

Small changes in proportions of limestone and shale have large effects upon the "burnability" of the raw mix; that is, upon the ease with which the mix can be burned to a satisfactory clinker. From the standpoint of production, and economy of fuel, ac-

curate control of composition is important, because periods of easy burning do not compensate for loss in production and high fuel consumption during periods of hard burning. From the standpoint of quality of the product, it may be stated that the character of the clinker is influenced both by composition and the heat treatment applied to the mix in the kiln. Variations in composition affect burnability, and therefore affect kiln operation. The combination of varying composition and the resulting variation in kiln operation interferes with the attainment of uniformity in the product. It is evident from these considerations that control of composition of the raw mix is a critical operation, requiring that the proportions of limestone and shale, or equivalent materials, be accurately controlled.

Since the early days of the industry it has been the practice to subject the raw mix to certain rapid chemical tests, to determine whether the mix is correctly proportioned or to indicate needed changes in proportions. With such control tests available, it is not necessary to proportion the raw materials precisely in a single operation. For example, in one type of operation the limestone and shale may be proportioned roughly to form preliminary raw mixtures, some with too much limestone and some with too little. These preliminary mixtures are then combined in suitable proportions to form the final raw mix fed to the kilns. Since the preliminary mixtures are fairly close to the desired composition, the degree of accuracy required in the second proportioning operation is much less than that which would be required if the raw materials were proportioned in a single operation. This procedure, and other procedures designed to eliminate the necessity of extremely precise weighing of raw materials, would be impossible without the control tests.

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Function of Rapid Control Tests

Rapid control tests have an important place in all methods of proportioning raw mixtures. To illustrate their function in a simple manner, let us assume that a plant has raw materials of the compositions indicated in the following table, and that they do not vary in composition. We will suppose that the mixture in the last column, made with 83.0 per cent lime-

RAW MATERIALS			
	Limestone A	Shale	Mix No. 1
SiO ₂	3.57	63.24	13.71
Al ₂ O ₃	1.53	15.78	3.95
Fe ₂ O ₃	1.64	5.32	2.27
CaO	49.71	2.12	41.62
MgO	1.20	1.12	1.19
Ignition loss	42.35	12.42	37.26
Carbonates	91.70	6.56	77.24

stone and 17.0 per cent shale, has been found to be satisfactory, and that it is proposed to make this mixture continuously.

It would be possible, of course, to make the desired mix continuously by precise weighing operations. However, because of the nature of the raw materials and the large quantities to be handled, it is difficult to maintain a high degree of precision in the weighing equipment. We seek precision, but must secure it in some other way. Starting without a knowledge of methods now in use, we might observe the first item in the analyses, the SiO₂ content. The desired mix contains 13.71 per cent SiO₂. It can be seen from the values for the raw materials that the SiO₂ content will be greater than 13.71 per cent if more than 17.0 per cent shale is present and that it will be less than 13.71 if less than 17.0 per cent shale is present. It would consequently be possible, even with crude weighing equipment, to obtain the desired composition by checking the SiO₂ content at various stages of the operation, continually working toward the required SiO₂ content. One advantage of selecting SiO₂ for this procedure would be that changes in SiO₂ content will clearly indicate corresponding changes in proportions of limestone and shale, because of the wide difference in SiO₂ content of the

limestone and shale. Referring to the analyses, we see that there are other constituents which could be chosen for the control test instead of SiO₂. The CaO content, ignition loss and carbonate content of the limestone and shale are far enough apart to offer possibilities. A choice is possible, and the basis for such a choice is the time required for the determination, and the simplicity of the method.

It should be understood from the foregoing discussion that the control test used in the proportioning operation makes it possible to secure accurate control of proportions with weighing equipment which is not capable of securing precise proportioning in a single operation. In fact, it is possible to secure accurate proportions by weight without any weighing operations in the plant. However, it cannot be said that precision in weighing is completely eliminated. It is necessary to weigh reagents when standardizing solutions for control tests, and to weigh samples for these tests. What we have done in the use of a control test is to transfer the precise weighing operation, and in some instances all of the weighing operations, from the plant to the laboratory, where conditions are more favorable for precision. This is the function of the control test. The particular constituent determined in the control test is not of primary interest. For example, if we were to seek to obtain 13.71 per cent SiO₂ in the mix in the operation we have been considering, it would not be because the SiO₂ content is of special interest, but because when this percentage is obtained, all the constituents are present in suitable proportions.

Control Tests in Common Use

The control test in most common use is the acid-alkali method, which is a determination of the amount of standard acid solution neutralized by a weighed sample of raw mix. The number of cubic centimeters of acid is multiplied by a factor to obtain the equivalent percentage of CaCO₃ in the mix. Since both CaCO₃ and MgCO₃ are neutralized by the acid, but MgCO₃ neutralizes 1.19 times as much acid as the same weight of CaCO₃, the

test value is the sum of the CaCO_3 and 1.19 times the MgCO_3 . In this study the test value obtained by the acid-alkali method will be referred to as the *carbonate content*.

At some plants the control test is a measurement of the volume of CO_2 gas liberated when a weighed sample of raw mix is treated with acid in a calcimeter. The volume of gas is converted to a weight basis, and expressed as percentage of CaCO_3 in the sample, by means of tables for taking into account both temperature and barometric pressure. MgCO_3 liberates CO_2 , and is included in the same manner as in the acid-alkali method. The test value is similarly referred to as the carbonate content.

In the analyses given in tables in this paper the carbonate content is obtained by calculation from the formula,

$$\text{Carbonates} = 1.7848 \times \text{CaO} + 2.4824 \times \text{MgO}$$

The carbonate content obtained by the acid-alkali or calcimeter methods may not agree with these theoretical values, since a small percentage of the CaO or MgO may be present in some form other than carbonate. In addition, some of the other constituents may have a small influence on the value obtained by the acid-alkali method. However, this does not interfere at all with the application of these methods when the test value to be obtained in a correctly proportioned mix is known.

Variations in Raw Material Composition

The function of control tests has been described with reference to an ideal condition, in which the raw materials do not vary in composition. In practice, cement raw materials are obtained from natural deposits, and these are somewhat variable in composition. As the limestone and shale received in the plant change in composition, the proportions required in the mix also change. These changes are usually accompanied by changes in the carbonate content required to secure a satisfactory mix composition. The carbonate content required at any given time to secure a desired composition will be referred to as the *carbonate requirement*. Carbonate determinations still serve in securing

accurate control of proportions, but the value sought must be adjusted from time to time to correspond with the carbonate requirement. The laboratory phase of the proportioning operation consequently involves two problems: to establish relations between the various constituents to be maintained continuously in the raw mix fed to the kilns; and to develop principles which may form a basis for methods of control in which the advantages of the speed and convenience of carbonate determinations are retained in operations in which the principal object is to secure desired relations between constituents. The first problem will be discussed briefly. The second problem involves the development of a method for determining the carbonate requirement, which is discussed in detail in Part II. The application of the principles to be brought out is an individual problem for each plant, because of differences in equipment and layout. To assist in planning a system of control suitable for a particular plant, application to typical processes will be discussed at some length in Part III.

Relations Sought in Composition Control

Since the early days of the industry various formulas have been devised to express relations to be sought in control of composition. In some cases these formulas have been empirical, while in others the formulas have expressed relations based upon theories of constitution of portland cement clinker, usually those generally accepted at the time. It is not the purpose of this paper to discuss the history of proportioning formulas, but to consider composition control on the basis of present ideas concerning the constitution of portland cement clinker. Although it is understood that further research may introduce some modifications,* par-

*Since this was written, a paper by M. A. Swayze has appeared, in which is shown that C_2F forms a complete series of solid solutions with a new compound, $\text{C}_6\text{A}_2\text{F}$. This series includes C_4AF . It has been found by the writer that expression of composition in these terms will not affect the formulas in this paper for estimating the carbonate requirement, nor the methods of control described. Mr. Swayze's paper appeared in the *American Journal of Science*, Vol. 244, No. 1, Jan., 1946, and Vol. 244, No. 2, Feb., 1946.

ticularly with reference to minor constituents, it may be stated that control of composition on the basis of present knowledge of the compounds formed from the major constituents has led to greater uniformity in kiln operation and in the quality of the clinker produced.

$$C_3S = 4.0710 \text{ CaO} - 7.6024 \text{ SiO}_2 - 1.4297 \text{ Fe}_2\text{O}_3 - 6.7187 \text{ Al}_2\text{O}_3 \quad (1)$$

$$C_2S = 7.6024 \text{ SiO}_2 + 1.0785 \text{ Fe}_2\text{O}_3 + 5.0683 \text{ Al}_2\text{O}_3 - 3.0710 \text{ CaO} \quad (2)$$

$$= 2.8675 \text{ SiO}_2 - 0.7544 \text{ C}_3\text{S} \quad (2a)$$

$$C_3A = 2.6504 \text{ Al}_2\text{O}_3 - 1.6920 \text{ Fe}_2\text{O}_3 \quad (3)$$

$$C_4AF = 3.0432 \text{ Fe}_2\text{O}_3 \quad (4)$$

At the present time the major constituents of clinker are believed to be combined in the form of tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$, dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$, tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and tetracalcium aluminoferrite, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. In the range of compositions encountered in portland cement clinker, magnesia is essentially uncombined. The formulas for the cement compounds may be abbreviated by using the symbols C, A, S, and F to represent CaO , Al_2O_3 , SiO_2 , and Fe_2O_3 , respectively. In the abbreviated form, the formulas of the compounds, in the order in which they are stated above, are C_3S , C_2S , C_3A , and C_4AF .

The percentages of the compounds may be calculated from the oxide composition of a clinker or cement. It is common knowledge, however, that two cements of practically identical calculated compound composition may behave differently. This may be due to the influence of minor constituents, which is not fully understood, to the presence of glass as a result of rapid cooling, or to some lack in our present knowledge of the reactions of the major constituents in the clinkering process, so that the effect of differences in heat treatment in the kiln is not understood. However, the calculated compound composition is related to the burnability of raw mixtures in such a way that when it is controlled within reasonable limits variations in burnability are small and the operation of the kiln is not disturbed. Uniform potential compound composition accompanied by uniform kiln operation leads to uniformity in the quality of the product.

The compound composition, calculated on the assumption of complete combination, will be referred to as the *potential composition*. The following equations for calculating potential composition will be used in all computations in this paper.

It will be observed that in the equations for C_3S and C_2S the constituents derived from limestone and shale are of opposite sign, and that the coefficients for CaO , Al_2O_3 , and SiO_2 are large. It is to be expected, then, that a small change in proportions of limestone and shale will have a large effect upon the potential C_3S and C_2S . An increase of 1.0 per cent in the percentage of limestone will increase the potential C_3S about 12 per cent, and reduce the potential C_2S about 11.5 per cent. The 0.5 per cent change in the total C_3S and C_2S is distributed among the other constituents, C_3A , C_4AF , and MgO , with only small changes in each. Thus it is seen that control of potential C_3S or C_2S is important, particularly since it is known that an increase in C_3S with a corresponding decrease in C_2S makes the mix more difficult to burn in the kiln. It may be mentioned further that the theoretical lime limit is attained when the potential C_2S is reduced to zero. From this it is easy to understand why the crude proportioning processes in the early days of the industry frequently led to periods in which the product was unsound. The trend in recent years toward higher C_3S compositions, to increase early strength, makes fine control of composition much more important than it was twenty years ago.

Since at most plants the sum of the potential C_3S and C_2S is nearly constant, it is usually unimportant whether a constant C_3S or C_2S is sought. If the raw materials vary in such a way that the sum of the two silicates varies considerably, and the C_2S is brought too low at times when controlling on the basis of potential

C_3S , it is a safer practice to seek a constant potential C_2S . Some operators prefer to maintain a constant C_3S/C_2S ratio. This offers no particular advantage when the sum of the silicates is fairly constant. When the sum of the silicates is variable, control of the C_3S/C_2S ratio is a safer practice than control of potential C_3S content. It amounts to a compromise between control of potential C_3S and control of potential C_2S .

An Outline of the Plan of Attack

Before entering into a detailed study of the methods of determining the carbonate requirement and applications to typical processes, it is desirable to obtain a view of the general features of the procedure to be described. In controlling proportions of raw materials, the chemist decides upon a carbonate content to be maintained in the mix until conditions indicate the need of a change, when a higher or lower carbonate content is selected. The value selected as a basis for controlling proportions will be referred to as the *holding point*, which is a term used in some cement plants. The general plan is to adjust the holding point so that it will follow changes in the carbonate requirement. This can be accomplished by determining the carbonate requirement once a day, or perhaps twice a day if it is found to be necessary. Through these determinations of the carbonate requirement and the corresponding adjustments of the holding point, the advantages of the speed and convenience of controlling proportions by carbonate determinations is retained in control operations for maintaining a constant potential C_3S or C_2S .

For the determination of the carbonate requirement, to be described later, a sample of the raw mix is analyzed, determining SiO_2 , Fe_2O_3 , Al_2O_3 , CaO , and ignition loss. The carbonate content is also determined by the rapid control method. This determination requires several hours, even with the most rapid analytical methods. It should be evident, then, that if the limestone and shale change in composition abruptly, determinations of the carbonate requirement will serve no useful purpose. To se-

cure good control of the proportioning operation the changes in raw material composition must be gradual, either naturally or through handling the raw materials in such a manner as to eliminate abrupt variations.

Definitions of Terms

Certain of the terms already mentioned, and others, will be used repeatedly in the discussion which follows. Some of these will be used in a more general sense, others in a more restricted sense, than that in which they are commonly understood. They are defined here in the sense in which they are used in this paper.

Limestone and Shale. Cement raw mixtures are composed principally, sometimes entirely, of calcareous and argillaceous materials. The calcareous material may be limestone, marl, oyster shells, etc. All these materials, used as a source of CaO , will be referred to as *limestone*. Similarly, the argillaceous material, supplying both SiO_2 and Al_2O_3 , and usually Fe_2O_3 , may be clay or shale. Such materials will be referred to as *shale*. These materials may be combined in nature in a single raw material, cement rock. Methods referring to limestone and shale apply also to cement rock. On the other hand, blast furnace slag, which supplies both calcareous and argillaceous constituents, offers special problems in control of composition which are not considered in this paper.

Iron Ore. Any material which is used as a source of Fe_2O_3 , such as iron ore, pyrites cinders, mill scale, etc., will be referred to as iron ore.

Sand. Any material added to the mix to increase the SiO_2 content will be referred to as sand.

Carbonates. The acid-neutralizing value of the mix, or the amount of CO_2 evolved by the mix in acid, is expressed as a percentage of $CaCO_3$. This will be referred to as the carbonate content, and is equal to $CaCO_3 + 1.19 MgCO_3$, as previously explained. It includes $MgCO_3$ expressed as $CaCO_3$.

Carbonate Requirement. The carbonate content which the raw mix should have to secure a desired potential C_3S or C_2S content.

Holding Point. The carbonate con-

tent selected by the plant chemist as the value to be maintained in the mix. The holding point may be changed from time to time, as indicated by changes in the carbonate requirement.

Complete Analysis. Analyses of raw mixtures are referred to as "complete analyses" if they include SiO₂, Fe₂O₃, Al₂O₃, CaO, and ignition loss.

Lag in Control. The delay in adjustment of proportions due to the time elapsing between proportioning the materials and the determination of carbonate content. For example, this will include the time required for material to pass from the proportioning point to the sampling point, the sampling interval, and the time required for the carbonate determination.

Preliminary Raw Mixtures. Mix-

tures approaching the desired raw mix composition, prepared for use in a second proportioning operation. Since a second proportioning operation is seldom used in the dry process, preliminary mixtures are usually in the form of a raw mix ground with water, commonly referred to as a slurry.

Potential C₃S or C₂S. The value obtained by applying equation 1 or 2 to the composition of a clinker, raw mix or raw material, expressed on an ignited basis. In the case of a raw material, such as limestone or shale, the calculated value may be several hundred per cent, and may be positive or negative. The value obtained is used in computations as though such percentages could actually be present.

Part II — Mathematical Study of the Problem

THE CARBONATE CONTENT of the raw mix is expressed on a raw, or unignited, basis, while the potential composition is expressed on an ignited basis. As the carbonate content is adjusted by changing the proportions of limestone and shale, the ignition loss also changes. It is evident, then, that the relation between the carbonate content of a raw mix and its potential composition is not linear. However, within the narrow range of compositions involved in preliminary raw mixtures, the relation is so nearly linear that the effect of changes in carbonate content on potential composition can be expressed in very

simple terms. This is also true of the relation between the percentage of limestone or shale and the potential composition.

Because of the practically linear relations involved, it is possible to start with a single limestone and shale, and a single mixture of them, and then study the effect of changes in proportions of the materials upon the carbonate content and upon the potential composition. Upon learning these effects we can devise a method of estimating the carbonate requirement.

For our purpose we can start with limestone A, shale, and raw mix No. 1, which were used previously in illus-

RAW MATERIALS		MIXTURES		Difference
Limestone A	Shale	Mix 1	Mix 1A	
Proportions of Raw Materials				
Limestone A		83.00	84.17	+1.17
Shale		17.00	15.83	-1.17
Oxide Composition (Unignited)				
SiO ₂	3.57	63.24	13.71	13.02
Al ₂ O ₃	1.53	15.78	3.95	3.79
Fe ₂ O ₃	1.64	5.32	2.27	2.22
CaO	49.71	2.12	41.62	42.18
MgO	1.20	1.12	1.19	1.19
Loss	42.35	12.42	37.26	37.61
Carbonates	91.70	6.56	77.24	78.24
				+1.00
Potential Composition*				
C ₃ S		56.45	70.67	+14.22
C ₂ S		20.07	6.53	-13.54
C ₃ A		10.57	10.06	-0.51
C ₄ AF		11.02	10.83	-0.19
MgO		1.90	1.91	+0.01

*Calculated by equations 1-4 from oxide analysis, ignited basis.

*Calculated by equations 1-4 from oxide analysis, ignited basis.

trating the function of control tests in proportioning raw mixtures. To demonstrate the effect of increasing the carbonate content 1.00 per cent; that is, from 77.24 to 78.24 per cent, we have calculated another mixture, No. 1A, which is shown with mix No. 1 in the preceding table.

Referring to the table, it is seen that an increase of 1.00 per cent in carbonate content increases the C_3S 14.22 per cent and lowers the C_2S 13.54 per cent. This refers to the particular raw materials used in making mixtures 1 and 1A, but it is typical of the results obtained in such computations with a wide variety of raw materials. In general, the increase in C_3S for a 1.00 per cent increase in carbonate content is approximately 14.5 per cent, and the decrease in C_2S about 13.5 per cent. Conversely, to obtain an increase of 1.0 per cent in potential C_3S , the carbonate content should be increased $1/14.5$, or 0.07 per cent. To obtain an increase of 1.0 per cent in C_2S , the carbonate content should be decreased $1/13.5$, or 0.074 per cent.

Calculation of the Carbonate Requirement

Since the change in carbonate content required to secure a 1.0 per cent increase in C_3S or C_2S is known, it is possible to calculate the carbonate requirement from the potential C_3S or C_2S content of a raw mix sample,* and its carbonate content. For example, let us suppose that a sample of mix No. 1 has been analyzed for determination of the carbonate requirement, with the results shown in the foregoing table. The carbonate content and potential C_3S are 77.24 and 56.45 per cent, respectively. If the C_3S sought in the control operation is 60.0 per cent, the C_3S content of the sample is 3.55 per cent too low. The carbonate requirement is then $77.24 + 0.07 \times 3.55$, or 77.49 per cent. The same result would be obtained if mix No. 1A, made from the same raw materials, had been sampled and analyzed for determination of the carbonate requirement. It should be observed that in sampling for determination of the carbonate requirement, all that is necessary is that the sample is composed of the raw mate-

rials in use at the time. It does not need to be a correctly proportioned mix. It is important to understand this, because it may sometimes be possible to secure early information concerning the carbonate requirement by taking grab samples for the purpose instead of samples collected by a continuous sampler for routine control of proportions.

The method of calculating the carbonate requirement may be expressed in equation form, as follows:

For control of potential C_3S :

$$P = p + 0.07(A - a) \quad (5)$$

For control of potential C_2S :

$$P = p + 0.074(b - B) \quad (6)$$

in which P = carbonate requirement

p = carbonate content of mix sample (as determined by rapid control method)

A = desired potential C_3S

a = potential C_3S in mix sample

B = desired potential C_2S

b = potential C_2S in mix sample

It should be observed that in determining the carbonate requirement the carbonate content of the mix should be obtained by the rapid control method. The carbonate requirement is then in the same terms, automatically compensating for the effect of constant errors in the control test. For example, it will compensate for the presence of insoluble CaO and MgO in the raw materials in use at the time.

Influence of Coal Ash and Stack Losses

As the raw mix passes through the kiln some of it is picked up by the kiln gases and is carried out through the stack. This introduces a change in composition, because the fine particles caught up by the gases flowing through the kiln are not of the same composition as the raw mix as a whole. In addition, when coal is used as fuel, the coal ash is deposited to some extent with the raw mix in the

*The potential C_3S or C_2S is calculated from a complete analysis of the raw mix. The sample must be prepared for analysis by treatment which will make it possible to decompose the sample in acid. The preparation of raw mix samples is discussed in Appendix A.

kiln and is brought forward to the burning zone with the raw mix, where it becomes a part of the clinker produced. As a result of the combined effect of coal ash and dust loss, or dust loss alone when gas or oil is used, the potential composition of the clinker is not identical with that of the raw mix fed to the kiln. The C_3S or C_2S sought in the mix should therefore be somewhat different from the value desired in the clinker. To determine what this difference should be, the potential compositions of the kiln feed and clinker may be compared during a period of typical operation. At one plant, for example, the C_3S sought in the mix is 13 per cent higher than the value desired in the clinker, while at another plant it is 6 per cent higher. In determining the carbonate requirement, the desired potential C_3S or C_2S used in the calculation should be the value sought in the mix, not the value sought in the clinker.

Influence of Changes in Limestone Composition

A detailed study of the influence of changes in composition of the raw materials is not needed, since control of raw mix composition by adjusting the holding point to correspond with the carbonate requirement takes care of the effects of changes in the raw materials. However, a brief study of the influence of changes in limestone composition will serve to demonstrate the need for such a system of control. It will also provide examples comparing the calculated carbonate requirement with the carbonate content of mixtures calculated from the limestone and shale compositions to obtain a desired C_3S content.

Tables 1 and 2 have been prepared for the purpose of comparing compositions of raw mixtures obtained from shale and various limestones, each a modification of limestone A. In Table 1, these raw mixtures are made to a constant carbonate content, and in Table 2 to a constant potential C_3S content. The raw material compositions in Table 2 are identical with those in corresponding columns of Table 1, and are repeated for convenience in considering raw mix compo-

sitions with reference to the limestone used. The tables are presented together to facilitate comparison of control based upon carbonate content with control based upon securing a constant potential C_3S .

The modifications in limestone A to obtain the remaining limestones in Tables 1 and 2 are as follows: In limestone B, $CaCO_3$ has been replaced by $MgCO_3$ to an extent sufficient to lower the CaO content 1.00 per cent. This results in a slightly higher ignition loss in limestone B. Limestone C is identical with limestone A on an ignited basis, but has a higher ignition loss. The compositions of limestones D and E require no comment.

In Table 1 each limestone has been combined with the shale to obtain a mixture with 77.24 per cent carbonates, the carbonate content of mix No. 1. In Table 2 each limestone has been combined with the shale to obtain a mixture with 56.45 per cent C_3S , the potential C_3S content of mix No. 1. For the purpose of studying the effects of changes in limestone composition it will be assumed that 56.45 per cent C_3S is sought in control of composition. Table 1 then indicates the variations in potential compositions to be expected when the limestone changes from A to B, A to C, etc., if the carbonate content is maintained constant without considering the changes in the limestone. On the other hand, Table 2 indicates the changes which will occur under the same conditions if the potential C_3S is maintained at 56.45 per cent. (The values in Table 2 are within 0.10 per cent of that value.)

Considering the change from limestone A to B, it will be seen that to maintain a constant potential C_3S the carbonate content should be raised from 77.24 to 77.88 per cent (mix No. 6), an increase of 0.64 per cent. If the need for this increase is not observed, and the carbonate content remains at 77.24 per cent, the C_3S content drops from 56.45 to 47.44 per cent (mix No. 2), that is, a decrease of 9.0 per cent. This is due to the fact that MgO , expressed as $CaCO_3$, is included in the carbonate content, but does not enter into the computation of C_3S . That is, the 77.24 per cent

TABLE 1—RAW MIXTURES PROPORTIONED TO CARBONATE
CONTENT OF RAW MIX NO. 1 (77.24 PER CENT)

	Limestone					Shale				
	A	B	C	D	E	A	B	C	D	E
(a) Composition of Raw Materials										
SiO ₂	3.57	3.57	3.51	4.57	3.57	63.24				
Al ₂ O ₃	1.53	1.53	1.50	1.53	2.03	15.78				
Fe ₂ O ₃	1.64	1.64	1.61	1.64	2.14	5.32				
CaO	49.71	48.71	48.85	48.71	48.71	2.12				
MgO	1.20	2.05	1.18	1.20	1.20	1.12				
Loss	42.35	42.50	43.35	42.35	42.35	12.42				
Carbonates	91.70	92.03	90.12	89.92	89.92	6.56				
(b) Percentages of Limestone and Shale										
Limestone	83.00	83.44	83.25	84.29	83.90					
Shale	17.00	16.56	16.75	15.71	16.10					
(c) Composition, Unignited Raw Mix										

TABLE 2—RAW MIXTURES PROPORTIONED TO POTENTIAL
C₃S CONTENT OF RAW MIX NO. 1 (56.45 PER CENT)

	Limestone					Shale				
	A	B	C	D	E	A	B	C	D	E
(a) Composition of Raw Materials										
SiO ₂	3.57	3.57	3.51	4.57	3.57	63.24				
Al ₂ O ₃	1.53	1.53	1.50	1.53	2.03	15.78				
Fe ₂ O ₃	1.64	1.64	1.61	1.64	2.14	5.32				
CaO	49.71	48.71	48.85	48.71	48.71	2.12				
MgO	1.20	2.05	1.18	1.20	1.20	1.12				
Loss	42.35	42.50	43.35	42.35	42.35	12.42				
Carbonates	91.70	92.03	90.12	89.92	89.92	6.56				
(b) Percentages of Limestone and Shale										
Limestone	83.00	82.70	84.59	84.79	84.79					
Shale	17.00	17.30	15.41	15.21	15.21					
(c) Composition, Unignited Raw Mix										

	Raw Mix No.								
	1	6	7	8	9	1	6	7	8
(a) Composition of Raw Materials									
SiO ₂	13.71	13.45	13.51	13.79	13.18	13.71	13.45	13.51	13.79
Al ₂ O ₃	3.95	3.89	3.89	3.77	4.24	3.95	3.89	3.89	3.77
Fe ₂ O ₃	2.27	2.25	2.23	2.22	2.65	2.27	2.25	2.23	2.22
CaO	41.62	40.99	41.02	41.39	41.21	41.62	40.99	41.02	41.39
MgO	1.19	1.90	1.17	1.19	1.19	1.19	1.90	1.17	1.19
Loss	37.26	37.52	38.18	37.64	37.53	37.26	37.52	38.18	37.64
Carbonates	77.24	77.88	76.12	76.82	76.50	77.24	77.88	76.12	76.82
(d) Potential Composition, Ignited Raw Mix									
C ₃ S	56.45	56.45	56.54	56.37	56.50	56.45	56.45	56.54	56.37
C ₂ S	20.07	19.15	20.01	20.88	17.88	20.07	19.15	20.01	20.88
C ₃ A	10.57	10.40	10.58	10.00	10.81	10.57	10.40	10.58	10.00
C ₄ AF	11.02	10.96	10.98	10.84	12.90	11.02	10.96	10.98	10.84
MgO	1.90	3.04	1.89	1.91	1.91	1.90	3.04	1.89	1.91

	Raw Mix No.					Raw Mix No.				
	1	2	3	4	5	1	2	3	4	5
(a) Composition of Raw Materials										
SiO ₂	13.71	13.89	12.71	13.49	12.65	13.71	13.89	12.71	13.49	12.65
Al ₂ O ₃	3.95	4.00	3.70	3.70	4.12	3.95	4.00	3.70	3.70	4.12
Fe ₂ O ₃	2.27	2.28	2.18	2.20	2.62	2.27	2.28	2.18	2.20	2.62
CaO	41.62	40.65	41.65	41.62	41.62	41.62	40.65	41.65	41.62	41.62
MgO	1.19	1.89	1.17	1.19	1.19	1.19	1.89	1.17	1.19	1.19
Loss	37.26	37.29	38.59	37.80	37.80	37.26	37.29	38.59	37.80	37.80
Carbonates	77.24	77.24	77.24	77.24	77.24	77.24	77.24	77.24	77.24	77.24
(d) Potential Composition, Ignited Raw Mix										
C ₃ S	56.45	47.44	73.20	62.49	67.27	56.45	47.44	73.20	62.49	67.27
C ₂ S	20.07	27.73	4.14	16.05	7.57	20.07	27.73	4.14	16.05	7.57
C ₃ A	10.57	10.75	9.97	9.77	10.43	10.57	10.75	9.97	9.77	10.43
C ₄ AF	11.02	11.07	10.80	10.77	12.81	11.02	11.07	10.80	10.77	12.81
MgO	1.90	3.01	1.91	1.91	1.91	1.90	3.01	1.91	1.91	1.91

carbonate content when limestone *B* is used means less CaO available for formation of C_3S than when limestone *A* is used. It may be noted here that at some plants the control test is a rapid determination of lime content, precipitating the lime as oxalate. In that case, magnesia is not included in the test value, and the effect of the change from limestone *A* to *B* is to increase the potential C_3S about 16 per cent. It is apparent that with either control test, variations in magnesia content may have considerable effect upon burnability of the raw mix if the holding point is not adjusted to take care of the variations when they occur.

It is possible to overcome the effect of abrupt variations in magnesia content by a method which will be presented in another paper. In the present paper it is assumed that changes in raw material composition occur slowly, either naturally or through methods of handling the materials. Under these conditions, determination of the carbonate requirement once a day will lead to appropriate changes in the holding point. For example, mix No. 2 was obtained by maintaining the same carbonate content as mix No. 1, and shows what will occur if the carbonate requirement is not known, and the holding point is consequently not adjusted to take care of the increase in MgO content. Mix No. 2 is 56.45-47.44, or 9.0 per cent too low in potential C_3S . Applying equation 5 to mix No. 2, the carbonate requirement is found to be $77.24 + 0.07 \times 9.0$, or 77.87 per cent. If the limestone changed in MgO content from limestone *A* to limestone *B*, a determination of the carbonate requirement would lead to raising the holding point 0.07×9.0 , or 0.6 per cent. This may be seen by referring to mix No. 6, Table 2, which has the desired C_3S content and has a carbonate content of 77.88 per cent.

In the change from limestone *A* to *C*, the ignition loss is increased 1.00 per cent, with no change in relative proportions of the other constituents. The carbonate content should be lowered from 77.24 to 76.12 per cent (mix No. 7) to maintain a constant potential C_3S . If the carbonate content is

not lowered, as it should be, the potential C_3S increases from 56.45 to 73.20 per cent (mix No. 3), an increase of 16.75 per cent. At the same time the potential C_2S is reduced to 4.14 per cent, making this a very hard burning composition. Changes in ignition loss may not appear to be a common source of error in proportioning, except in plants using marl, in which the per cent of organic matter fluctuates considerably. It should be noted, however, that moisture which may be present is a part of the ignition loss. From this it is seen that failure to dry test samples completely, or to the same moisture content, may have a disturbing effect upon control operations.

The carbonate requirement, calculated from the compositions of raw mixtures in Table 1 are shown below, with the carbonate content of mixtures in Table 2 which were obtained from the corresponding limestones when proportioning on the basis of potential C_3S .

Mix No.	Carbon-ates	C_3S	Carbon-ate Requirement*	Mix No.	Carbon-ate Content
2	77.24	47.44	77.87	6	77.88
3	77.24	73.20	76.07	7	76.12
4	77.24	62.49	76.82	8	76.82
5	77.24	67.27	76.48	9	76.50

*Calculated by equation 5.

It will be observed that the values obtained by equation 5 are very close to the carbonate content actually required for a constant C_3S , closer than the accuracy obtainable in the carbonate determination.

Effect of Iron Ore or Sand Additions on the Carbonate Requirement

In recent years there has been a demand for cements with lower C_3A content, or lower C_3A and C_4AF content, than can be made from limestone and shale, or equivalent materials commonly available at cement plants. These cements are used for special purposes, such as massive concrete construction where low heat of hydration is desired and concrete exposed to the attack of sulphates. The production of these cements requires the addition of high-iron or siliceous material, or both, to the raw mix. For convenience, the high-iron and sili-

ceous materials will be referred to as iron ore and sand, respectively.

When iron ore or sand is added to a raw mix, the potential C_3S is lowered and the potential C_2S is increased. Since the addition of limestone has the opposite effect, the effect of the iron ore or sand on either the C_3S or C_2S may be balanced by adding a suitable quantity of limestone. The problem, then, is to determine the change in carbonate content when the iron ore or sand addition has been made to a correctly proportioned mix, with sufficient limestone added at the same time to leave the potential C_3S or C_2S unchanged. For example, if control is based upon maintaining a desired potential C_3S in the mix, the "correctly proportioned mix" has the desired potential C_3S , and its carbonate content is the carbonate requirement determined before the change in proportion of iron ore or sand.

The effect of a change in proportion of iron ore or sand on the carbonate requirement may be found from the following equation:

$$F = \frac{1}{100} \left[p_1 - p + \frac{S_1(A - A_1)(p_2 - p)}{S_2(A_2 - A)} \right] \quad (7)^*$$

in which F = factor representing the increase in carbonate requirement for each per cent increase in iron ore or sand

A = C_3S (or C_2S) sought in control

p = carbonate requirement (before change in proportion of iron ore or sand)

A_1 = C_3S (or C_2S) of iron ore or sand

p_1 = carbonate content of iron ore or sand

S_1 = 100 — ignition loss of iron ore or sand

A_2 = C_3S (or C_2S) of limestone

p_2 = carbonate content of limestone

S_2 = 100 — ignition loss of limestone

As indicated above, equation 7 may be applied in control to secure a desired C_2S . The quantities A_1 and A_2 require some explanation. They are

obtained by applying equation 1 or 2 to the oxide composition, ignited basis. Since the materials to which they refer are not of portland cement composition, the values obtained appear unreasonable. However, they have a definite significance in mix computations. For example, the C_3S value of a limestone and a shale may be +375 and —645 per cent, respectively. These values indicate that a substitution of 1.0 per cent limestone in place of 1.0 per cent shale, ignited weight basis, raises the potential C_3S in the mix $3.75 - (-6.45)$, or 10.2 per cent. Because of their definite significance with reference to the effect which they have on the potential C_3S or C_2S in raw mixtures, these apparently unreasonable values of A_1 and A_2 are used in mix computations as though they represented real percentages of these compounds.

Equation 7 is too complex for use in routine mix control operations. Furthermore, it would be unusual to have complete analyses of the limestone and iron ore or sand in actual use at the time that an estimate of the change in carbonate requirement is needed. We must therefore examine the possibility of simplifying the formula by substituting approximate analyses of these materials for analyses representing accurately the materials in use at the time. It might seem that this would be impossible in the case of limestone, since this is present in greatest quantity in the mix. However, it should be noted that the equation is based on the idea that the limestone and iron ore or sand is added to a correctly proportioned mix, represented by A and p . This takes care of the shale and all the limestone except that added to balance the iron ore or sand. Any error due to differences between the average limestone composition and the composition of the limestone in actual use at the time applies only to the comparatively small quantity of limestone required to balance the iron ore or sand. From these considerations it appears feasible to simplify equation 7 by substituting the desired C_3S content for A , and substituting values obtained from average compositions of lime-

*Equation 7 is derived in Appendix B.

stone and iron ore or sand for the quantities designated by subscripts.

Since the simplified formula is based upon average compositions of limestone and iron ore or shale in use at the plant, it is impossible to present a formula here for general use. However, the method of deriving such a formula may be shown by a specific example. Let us assume that at a particular plant the average compositions of the limestone and iron ore are those given in the following table.

	Iron Ore	Limestone A
SiO ₂	13.34	3.57
Al ₂ O ₃	5.32	1.53
Fe ₂ O ₃	66.43	1.64
CaO	4.57	49.71
MgO	0.79	1.20
Ignition loss	9.55	42.35
Carbonates	$p_1 = 10.12$	$p_2 = 91.70$
C ₃ S	$A_1 = -236$	$A_2 = 282$
100—ignition loss .	$S_1 = 90.45$	$S_2 = 57.65$

Substituting in equation 7,

$$F = \frac{1}{100} \left[10.12 - p + \frac{90.45(50 + 236)(91.70 - p)}{57.65(282 - 50)} \right]$$

$$F = \frac{1}{100} \left[10.12 - p + \frac{90.45 \times 286(91.70 - p)}{57.65 \times 232} \right]$$

$$F = 1.87 - 0.0293p \quad (8)$$

For all values of the carbonate requirement, p , which are encountered in practice, the value of F obtained from equation 8 is negative; that is, an increase in the proportion of iron ore in the mix lowers the carbonate requirement, and vice versa. To illustrate the use of equation 8, let us assume that the carbonate requirement is 76.2 per cent and that the proportion of iron ore is to be reduced from 3.5 per cent to 1.0 per cent, that is, a reduction of 2.5 per cent. The factor F is $1.87 - (0.0293 \times 76.2)$, or -0.363 . The carbonate requirement should therefore be increased 0.363×2.5 , or 0.91 per cent, that is, from 76.2 to 77.1 per cent.

Part III — Application to Typical Processes

A VARIETY OF PROCESSES are used in preparing raw mixtures for the manufacture of portland cement. From the standpoint of the procedure to be followed in applying determina-

Simplified formulas, derived in the same manner as equation 8, are reasonably accurate for all changes in proportion of iron ore encountered in practice. This is a result of the fact that large percentages of iron ore are not used, and also that the amount of limestone required to balance the effect of the iron ore is small. It is because of the small amount of limestone required that the value of F is negative. On the other hand, sand or equivalent material is used in larger quantities, and from four to six times its weight is needed to balance its effect on potential C₃S or C₂S. Equation 7 applies accurately to both iron ore or sand, but a simplified equation derived from it in the same manner as equation 8 is not as accurate in the case of sand. It will be satisfactory for small changes in proportions of sand, but should not be applied to large changes. The maximum change in proportion of sand to which such an equation may be applied will depend upon the extent to which the limestone and sand compositions vary from the compositions used in deriving the equation. The limit cannot be established theoretically. However, since a sample is taken after the change in proportion of sand, for a determination of the carbonate requirement, the maximum change in proportion of sand to which the equation may be safely applied will be learned by observation.

When both iron ore and sand are used, and the proportions of both are changed simultaneously, the effects of these changes can be estimated separately and then combined. For example, if the change in proportion of sand requires an increase of 1.8 per cent in the carbonate requirement, and the change in proportion of iron ore requires a decrease of 0.7 per cent, the net change in the carbonate requirement is an increase of $1.8 - 0.7$, or 1.1 per cent.

tions of the carbonate requirement in control of raw mix composition, they may be classified as follows:

1. *Continuous proportioning processes*, in which the crushed raw mate-

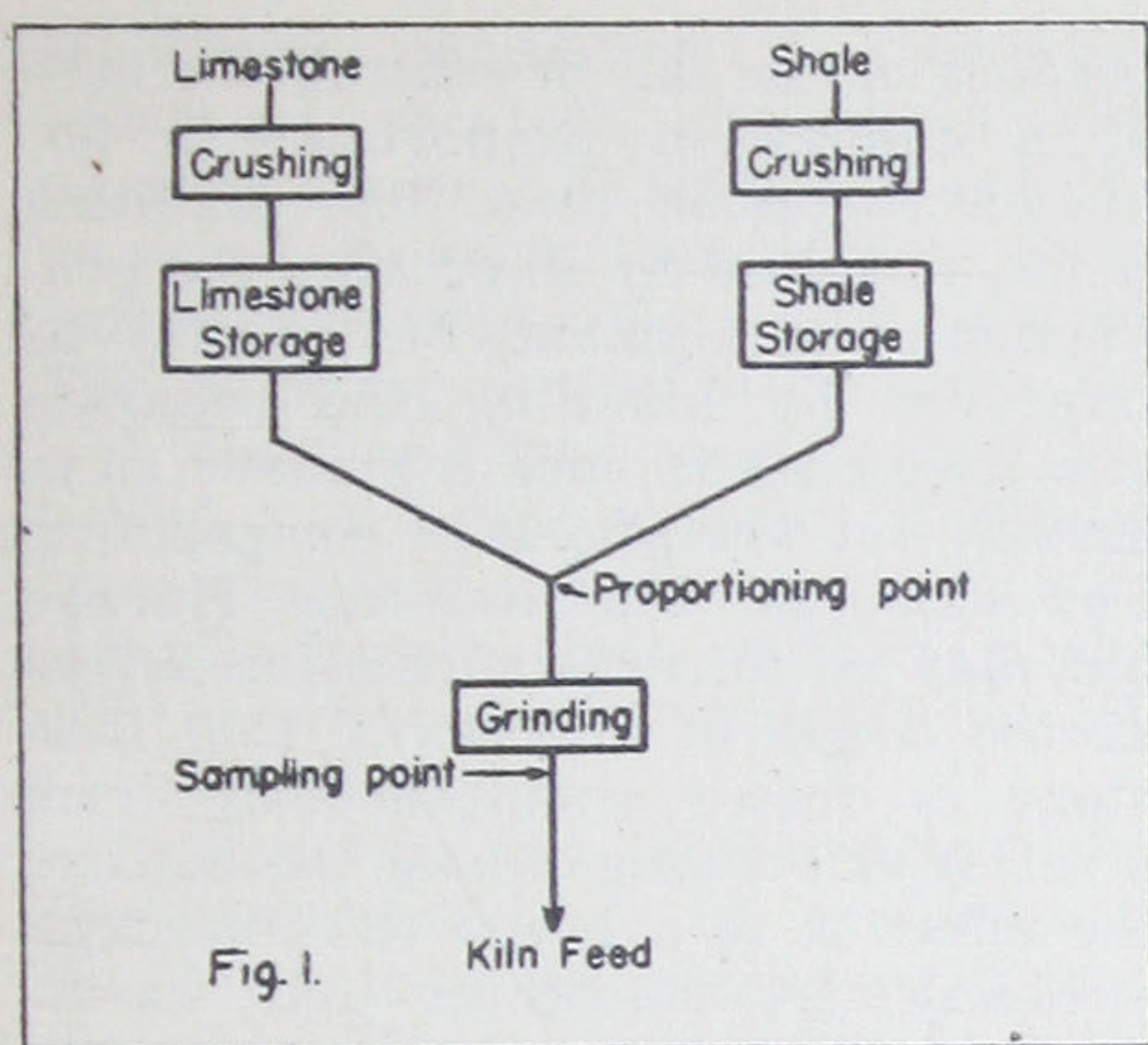


Fig. 1: Continuous proportioning process with no blending

materials move in separate streams toward a common point at which they are combined into a single stream, as shown in the flow diagram, Fig. 1. This is the only proportioning operation, the remaining operations being concerned with reduction of the mixture to a desired degree of fineness. In these processes the raw mix is usually handled in a dry condition. Control of composition in the single proportioning operation is usually unsatisfactory, and it has consequently become a common practice to blend the ground raw mixture, as shown in the flow diagram, Fig. 2. The blending

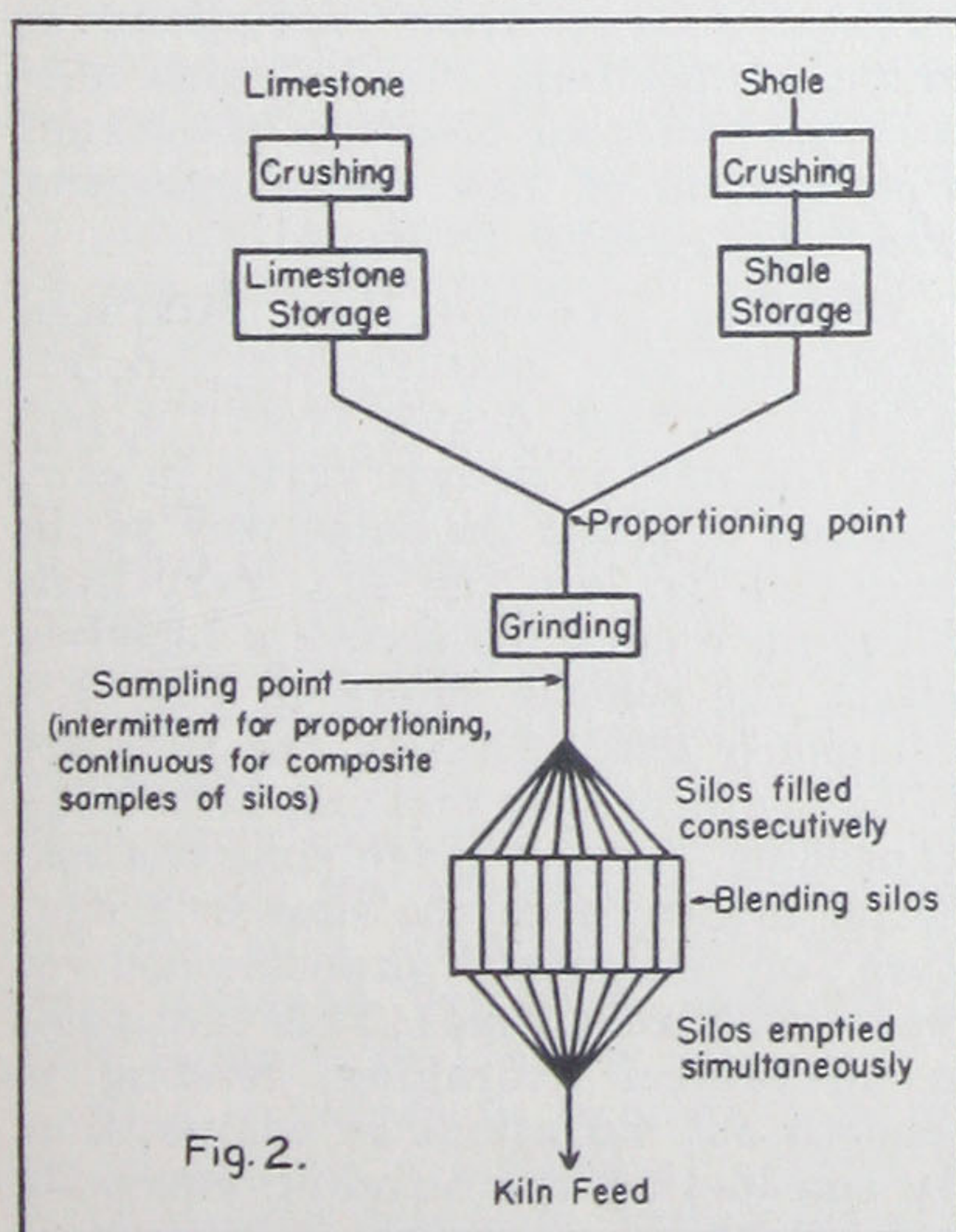


Fig. 2: Continuous proportioning process with blending

operation, which will be discussed in more detail later, smooths out variations in composition.

2. *Two-stage proportioning processes.* In these processes the first stage is a continuous proportioning process of the type shown in Fig. 1. The product of this stage is proportioned again in a second stage, which is a batch process. Only a few dry process plants use two-stage proportioning. It is commonly used in the wet process, in which the raw mixture is ground wet, forming a slurry. The flow diagram of a typical two-stage process is shown in Fig. 3.

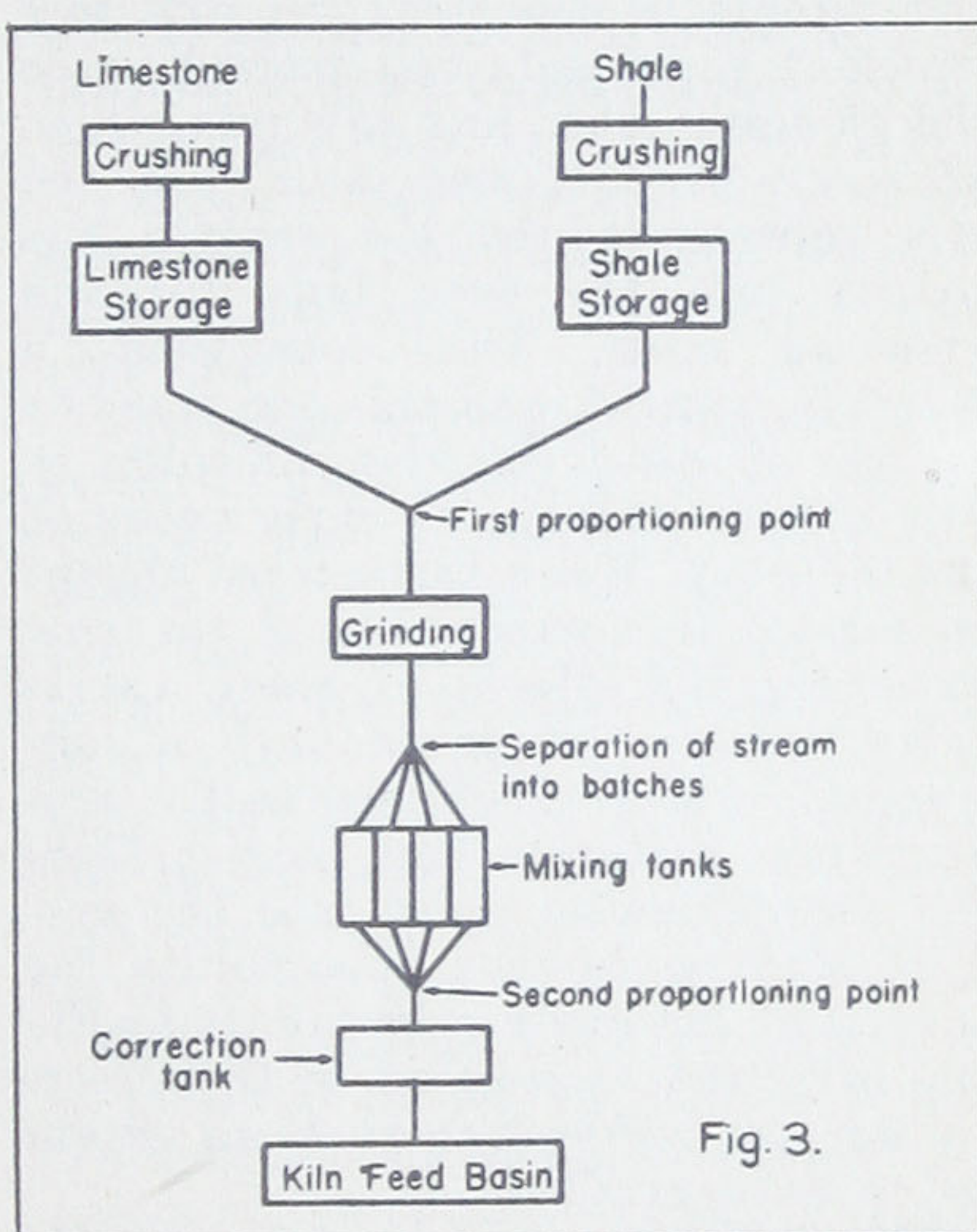


Fig. 3: Two-stage process (wet)

In a few wet process plants having mixing tanks of large capacity, samples of the entire quantity of slurry in a tank are taken at intervals while the tank is being filled. The carbonate contents of these samples are used as a basis for determining the proportions of limestone and shale or equivalent materials, at the first proportioning point (Fig. 3). This process differs from that shown in Fig. 3, since the desired carbonate content is obtained when each tank is filled, so that each mixing tank is also a correction tank. Although the actual proportioning operation is carried on at only one point, the process is equivalent to a two-stage proportioning process.

The Continuous Proportioning Process

Because of the difficulty of obtaining representative samples of raw mixtures in the crushed state, samples for control of the proportioning operation are taken from the discharge of the grinding mills, as shown in Fig. 1 and 2. As a result, the sample does not necessarily represent the product of the proportioning operation at the time the sample was taken, but represents the conditions at the proportioning point at an earlier time. By the time that the carbonate content of the sample is reported, the raw mix which it represents has passed on to the blending silos, and raw mix which has been proportioned later than the mix represented by the sample has passed into the feed bins for the grinding mills. This constitutes a "lag" in control, and this lag was the source of much of the difficulty in raw mix control in the early years of the industry. When there were abrupt variations in composition of the raw materials the effects of these variations were not observed until a considerable quantity of incorrectly proportioned material had passed from the proportioning point into the system, with no further opportunity for correction. In modern installations the lag in control is reduced, or the effects of lag are reduced to such an extent as to be negligible.

The lag in control may be reduced by reducing the capacity of feed bins for the grinding mills. The type of grinding equipment may also play a part in increasing or decreasing the lag in control. At some plants in which a large number of mills are used, the operation of one of the mills is conducted in such a manner as to reduce the lag, for sampling, while the remaining mills are operating on the same material without reference to reducing the lag.

Reduction of the Effect of Lag in Control. Assuming that the proportioning equipment is reliable, the effect of lag in control is due to variations in composition of the raw materials; that is, a change in composition of the raw materials may alter the carbonate content of the mix at the proportioning point. However,

because of the lag in control, the need of a change in proportions is not known for some time. The condition is not remedied by improving the proportioning equipment, but it may be improved by handling the separate raw materials in such a manner as to smooth out variations in composition. For example, the limestone storage bin may be filled in successive layers at the angle of repose. If the limestone is drawn simultaneously from a series of openings along the bottom, the effect is to average the limestone mechanically, smoothing out variations in all the constituents present. This procedure not only smooths out the variations in carbonate content, but also smooths out variations in the carbonate requirement. As a result, it practically eliminates one of the greatest sources of difficulty in controlling the carbonate content with reference to the holding point, and also makes it possible to use determinations of the carbonate requirement effectively in setting the holding point.

If only one raw material is blended by an operation such as that described above, the limestone is the better choice, since in most instances variations in limestone composition disturb control of potential C_3S and C_2S to a greater extent than variations in shale composition. Plants which have adopted limestone blending have found that control of raw mix composition has been greatly improved.

Blending Ground Raw Mixtures. When dry raw mixtures are fed into a silo, and then drawn from the bottom, the mix as drawn varies in composition in about the same way as the material fed into the silo. Very little blending occurs. To secure a blending effect, the scheme shown in Fig. 2 is commonly used. That is, the silos are filled consecutively and emptied simultaneously. At any given time the material drawn from the silos is a mixture of materials proportioned at widely different times. This constitutes a mechanical averaging, tending to smooth out variations in composition. In considering the blending effect obtainable from a group of silos it is necessary to consider composition variations of two kinds: (1) short swing

variations, occurring at intervals which are short in comparison with the time required to fill a silo, and (2) long swing variations, which occur during a considerable period of time. The blending operation smooths out both short and long swing variations, but in a different manner. Formulas for estimating the blending effect obtainable from a given number of silos may be misapplied if this difference is not understood.

In applying the mathematical theory of probabilities to problems of this kind, it is convenient to express the variability in composition in terms of standard deviation. Let us suppose that N silos are being filled consecutively and emptied simultaneously. The carbonate content of the entering stream varies in short swings, but there is no difference in the average composition in the individual silos, since a constant holding point has been maintained. In that case the standard deviation of the material drawn from the silos will be equal to the standard deviation of the entering stream divided by $\sqrt{N}$.

In this study we are concerned with the changes to be made in the holding point to maintain a constant potential C_3S or C_2S content, within reasonable limits. If the holding point is changed between silo fillings, these changes may be regarded as long swing variations. The silos differ in average carbonate content, and each is subject to short swing variations. If the previous method of estimating the blending effect is applied to the deviations from the general average for the contents of all the silos, a correct estimate of the blending effect will not be obtained. Instead, the deviations of the stream entering each silo should be the deviations *from the average for that silo*. Assuming that there are N silos, with the standard deviations identical, the standard deviation of the material drawn from all the silos simultaneously will be the standard deviation obtained in this manner, divided by $\sqrt{N}$.

This principle is important in its bearing upon a method of control to be described presently, and so we propose to emphasize it by an example in which the materials in the silos are widely different in composition. Let

us suppose that two silos are filled, one with material containing 85 per cent carbonates, the other 65 per cent, so that the average is 75 per cent. The standard deviation during the filling is assumed in each case to be 0.7 per cent, determined from the deviations from 85 and 65 per cent, respectively. The stream drawn from the silos simultaneously will contain 75 per cent carbonates, with a standard deviation of $0.7/\sqrt{2}$, or about 0.5 per cent. In view of the wide difference in carbonate content for the two silos, it must be assumed that they are drawn at such uniform rates that further deviations are not introduced in this operation. It may be seen from this extreme case that it would be absurd to measure deviations in the stream entering the individual silos from the general average, 75 per cent, for the two silos.

From the principles discussed, it is evident that blending after proportioning has limitations. Nine silos would be required to reduce variations to a third of the original variations, and sixteen silos to reduce them to a fourth. It may be of interest to note that eight silos would suffice in the latter case, if the blended material from four silos is blended again in the other four.

Other methods, such as circulation of material in the blending silos, and the introduction of air through porous plates at the bottom of the silo to give the dry mix the flow characteristics of a liquid, are sometimes used.

Due to limitations of the blending which may be accomplished, it is important that proportioning before blending should be sufficiently accurate to result in satisfactory uniformity in the blended product. In some instances blending silos have been installed with the idea that they will eliminate variations in raw mix compositions to a greater extent than is possible. In that case, the results are disappointing, and it then becomes necessary to use the blending silos as storage silos for a second proportioning operation; that is, when it is necessary to select pairs of silos to supply high- and low-lime mixtures to be combined to form a desired mix, the silos are not blending silos, but are used as sources of material for a sec-

and proportioning operation.

In practice, the blending operation is continuous. That is, the filling and emptying of the silos are going on simultaneously. To secure the greatest blending effect, as many silos as possible should be drawn at one time. The blending effect of eight silos cannot be obtained if only four are drawn at a time.

In describing the blending operation it was assumed for the purpose of illustration that the purpose in control is to maintain a constant carbonate content and that the blending operation smooths out deviations from that constant value. However, if the carbonate requirement changes, the holding point should be changed accordingly. If the carbonate content is maintained reasonably close to the carbonate requirement, the mix drawn from the blending silos may vary in carbonate content to a greater extent than when the holding point is not changed from time to time. However, the deviations from the carbonate requirement will be reduced by the blending operation.

Two types of blending operation have been considered: (1) blending the separate raw materials; and (2) blending the ground raw mix. The principle is the same, but the purpose is different. The first operation is intended to improve control of composition in the proportioning operation. The object of the second operation is to smooth out errors in proportioning after they have occurred. Both types may be employed to advantage.

Sampling for Control of the Proportioning Operation. The lag in control should be taken into account in judging the significance of tests on samples of the ground raw mix; that is, it should be borne in mind that the sample does not represent the proportioning operation at the time, but at a previous time. For example, if the time between proportioning and sampling is three hours, a sample taken at the mill discharge represents the condition at the proportioning point three hours earlier. If samples are collected from a continuous sampler at two-hour intervals, the sample represents the average condition at the proportioning point during a period between three and five hours earlier

than the time at which the sample is collected. The time intervals mentioned are not intended to represent plant practice, but serve to illustrate the importance of reducing the lag in control by collecting samples intermittently, rather than continuously, for a check on the proportioning operation. This applies particularly to continuous proportioning processes. Samples may be collected continuously for other purposes, for example, to obtain a composite sample of the raw mix in a silo or tank while it is being filled.

Selection of Holding Points in a Continuous Proportioning Process. It was pointed out previously that blending silos for ground raw mixtures do not eliminate short swing variations in composition but merely reduce them to a fraction of the deviations in the stream entering the silos. On the other hand, long swing variations caused by changes in the holding point are almost completely eliminated. This provides a basis for two methods of controlling the potential C_3S or C_2S content. In the first method to be considered, the approach to the carbonate requirement is in the proportioning operation, through determinations of the carbonate requirement daily, or twice a day if necessary, and adjustment of the holding point to correspond with it. In this method, efforts are in the direction of maintaining a carbonate content close to the carbonate requirement before the blending operation. In the alternate method, to be described presently, the approach to the carbonate requirement is in the blending operation.

In the first method, in which the approach to the carbonate requirement is in the proportioning operation, the holding point is adjusted to correspond with the carbonate requirement. In discussing the procedure it will be assumed that the raw materials vary slowly in composition, either naturally or through the manner in which they are handled. In that case, the carbonate requirement will vary slowly, so that the high and low points are several days apart. In the periods between these points the carbonate requirement is steadily increasing or decreasing. Such trends should be observed, and holding points

selected to follow these trends. Suppose, for example, that the carbonate requirement is reported on successive days as 76.5, 75.7 and 75.0 per cent. If these values are selected as holding points on the three days, the carbonate content will be the same as the carbonate requirement at the beginning of each day, but will exceed it for the remainder of the day. If there is an upward or downward trend in the carbonate requirement, the holding point should be adjusted from time to time during the day, to follow the trend.

In following the trend of the carbonate requirement, it should be borne in mind that the value reported is not the value at the time of reporting, but refers to an earlier time. For example, the sample used for the determination may represent material proportioned five or six hours before the report. If the carbonate requirement is plotted against time, as a means of following the trend, it should refer to the estimated time of proportioning. During periods in which the trend is definitely downward or upward, the holding points can be kept quite close to the carbonate requirement. However, with the value determined only once a day, it may be difficult to judge when a high or low point is approached. It is at these times that the holding point may fail to approach the carbonate requirement as closely as may be desired. With adequate blending facilities these deviations can be reduced to such an extent that they are negligible.

Alternate Method. When the carbonate requirement varies too rapidly to permit satisfactory estimates of the trend in the carbonate requirement it is necessary to adopt a method in which these estimates are not needed. The alternate method now to be described is based upon the fact that when adequate blending of the raw mix is provided it is only necessary that the *average* carbonate content should coincide with the *average* carbonate requirement. It should be understood that these averages refer to the total quantity of raw mix in the series of blending silos at any given time. When this condition is maintained, the function of the blending operation is to smooth out the short

swing variations in the difference between the carbonate content and the carbonate requirement. The method is described as follows.

Samples are taken at regular intervals at the sampling point shown in Fig. 2, for controlling operations at the proportioning point. At the same time a continuous sampling device is in operation to secure a composite sample of the stream discharged into each silo. When a silo is filled, the composite sample is used for determination of the average carbonate content and the average carbonate requirement of the silo contents. The difference between these values is the excess or deficiency of carbonates, as compared with the carbonate requirement.

Following this procedure for each silo, a record of the excess or deficiency in each silo may be kept, with the accumulative total in another column. In calculating the accumulative total any excess is added, and any deficiency subtracted. By selecting holding points to maintain the excess or deficiency of carbonates in the accumulative total as close to zero as possible, the proportioning operation is controlled to produce at most only a negligible excess or deficiency in the average composition of the entire series of silos. The carbonate content of the finished raw mix may vary, but these variations will for the most part be due to variations in the carbonate requirement, and are therefore not a matter of concern.

Blending silos frequently differ in capacity. The interstices between circular silos are commonly used, and these are of much smaller capacity than the circular silos. In such cases the excess or deficiency in each silo should be expressed in pounds, barrels or tons. For example, if a silo contains 1000 tons of raw mix, and the excess of carbonates is 1.3 per cent, this is equivalent to 1000×0.013 , or 13 tons excess carbonates.

The Two-Stage Proportioning Process

In the two-stage process the first stage is a continuous proportioning process supplying tanks of slurry to

be proportioned in batches in the second stage. At some plants the first proportioning operation is performed roughly, with no effort to produce preliminary mixtures close to the desired composition, while at others weighing devices are used to obtain fairly accurate control. In either case the desired composition can be obtained in the slurry fed to the kilns, but there is a difference in the degree of accuracy required in the second stage. If the preliminary raw mixtures (slurries) are close to the desired composition, the effects of errors in percentages of the slurries in the final mixtures are small. On the other hand, rough proportioning in the first stage introduces the necessity of accuracy in the second stage. In describing methods this difference in conditions will be considered.

In most instances slurry tanks must be released for the proportioning operation too rapidly to permit complete analysis of each tank of slurry. The second proportioning operation is consequently an operation for control of the carbonate content. If the carbonate requirement is determined at suitable intervals, and the holding point selected accordingly, the potential C_3S or C_2S is controlled within reasonable limits. Some plants have a sufficient number of tanks to permit complete analysis of each tank before release. Under these conditions potential composition is under direct control. Methods of performing the necessary computations for this type of operation are described in Part IV. In this section it will be assumed that complete analyses of the individual tanks of slurry are not available.

Computation of proportions of slurry to obtain a desired carbonate content is not difficult. To illustrate, let us assume that the test values for two tanks of slurry are as indicated below, and that the holding point is 73.2 per cent carbonates.

	Tank No. 1	Tank No. 2
Total carbonates (titration)	85.6	68.2
Per cent moisture . . .	32.7	39.4
Deviation from holding point	+12.4	—5.0

On the last line the deviations from the holding point are shown. These values, taken in reverse order, represent the relative proportions of slurry, on a dry weight basis, required to obtain 73.2 per cent carbonates in the mixture. That is, 5.0 parts by weight of slurry No. 1 and 12.4 parts by weight of slurry No. 2, dry weight basis, will give the required composition. These may be converted to a relative slurry volume basis by multiplying each of these relative weights by a factor obtained from Table 3. In these cases the relative volumes are obtained as follows:

	Rel wt., dry basis	Factor (Table 3)	Rel. Vol.
Slurry No. 1	5.0	$\times 1.10$	= 5.50
Slurry No. 2	12.4	$\times 1.31$	= 16.24

Let us suppose that the tanks are of the same diameter and that the depth of available slurry in each is 30 ft. Since slurry No. 2 is used in greater quantity, the entire 30 ft. may be used to empty the tank for further operations. The number of feet of slurry to be drawn from tank No. 1 is found as follows:

$$\frac{30 \times 5.50}{16.24} = 10.16 \text{ ft., or } 10 \text{ ft., } 2 \text{ in.}$$

Considering the preliminary raw mixtures on a dry basis, the effect of errors in proportions is proportional to the difference between the carbonate contents of the two materials. In this case the difference is $85.6 - 68.2$, or 17.4 per cent. It will be noted that this is the same as the sum of the relative weights, as obtained directly from the deviations from the desired carbonate content. An error of 1.0 per cent in proportions of the two materials will cause an error of 0.174 per cent in the carbonate content of the mixture. For example, the percentages of slurries No. 1 and 2 on a dry basis are $100 \times 5.0/17.4$ and $100 \times 12.4/17.4$, or 28.74 and 71.26 per cent, respectively. If the actual amounts used are 29.74 and 70.26 per cent, the carbonate content of the mix will be $73.2 + 0.17$, or 73.37 per cent. From this it may be seen that accuracy in measuring slurry volumes is required to control the carbonate content within 0.2 per cent. Because of

the physical condition of raw mix slurry, it is difficult to measure volumes with a high degree of accuracy. It is therefore good practice to test the mixture for carbonate content, and to make such adjustments as may be required. The calculation of quantities is therefore intended only to secure an approximation to the desired composition.

When the slurries to be combined are close to the desired composition, the effect of errors in proportioning are comparatively small. For example, if one slurry is 2.0 per cent too high in carbonate content, and the other 2.0 per cent too low, the sum of the deviations is 4.0 per cent. An error of 1.0 per cent in proportions of the two slurries, on a dry weight basis, will introduce an error of only 0.04 per cent in the carbonate content of the mixture. In such cases it may be possible to combine the slurries in the calculated quantities, with-

out depending upon further adjustments based on determinations of the carbonate content of the mixture. If the moisture contents of the slurries are not far apart, the relative proportions on a dry basis may be taken also as relative proportions on a volume basis, without applying the factors in Table 3. These are advantages secured by accurate proportioning in the first stage.

It may be noted that in Table 3 it is assumed that the specific gravity of the dry raw mix is 2.65. This is an estimate, but does not necessarily fit every case. In addition, the accuracy of the conversion is impaired by the presence of entrained air in the slurry. However, if the calculated quantities of slurry are regarded as approximate, to be checked when necessary by tests of the mixtures of slurry, the factors may be regarded as being generally applicable.

TABLE 3—FACTORS FOR CONVERSION OF RELATIVE DRY WEIGHTS
TO RELATIVE VOLUMES OF SLURRY*

Per-cent moisture	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
30	1.03	1.03	1.03	1.03	1.04	1.04	1.04	1.04	1.05	1.05
31	1.05	1.05	1.06	1.06	1.06	1.06	1.07	1.07	1.07	1.08
32	1.08	1.08	1.08	1.09	1.09	1.09	1.10	1.10	1.10	1.10
33	1.11	1.11	1.11	1.12	1.12	1.12	1.12	1.13	1.13	1.13
34	1.14	1.14	1.14	1.14	1.15	1.15	1.15	1.16	1.16	1.16
35	1.16	1.17	1.17	1.17	1.18	1.18	1.18	1.19	1.19	1.19
36	1.20	1.20	1.20	1.20	1.21	1.21	1.21	1.22	1.22	1.22
37	1.23	1.23	1.23	1.24	1.24	1.24	1.25	1.25	1.25	1.26
38	1.26	1.26	1.27	1.27	1.27	1.28	1.28	1.28	1.29	1.29
39	1.29	1.30	1.30	1.30	1.31	1.31	1.31	1.32	1.32	1.32
40	1.33	1.33	1.34	1.34	1.34	1.35	1.35	1.35	1.36	1.36
41	1.36	1.37	1.37	1.37	1.38	1.38	1.39	1.39	1.39	1.40
42	1.40	1.40	1.41	1.41	1.42	1.42	1.42	1.43	1.43	1.44
43	1.44	1.44	1.45	1.45	1.46	1.46	1.46	1.47	1.47	1.48
44	1.48	1.48	1.49	1.49	1.50	1.50	1.50	1.51	1.51	1.52
45	1.52	1.52	1.53	1.53	1.54	1.54	1.55	1.55	1.55	1.56
46	1.56	1.57	1.57	1.58	1.58	1.59	1.59	1.59	1.60	1.60
47	1.61	1.61	1.62	1.62	1.63	1.63	1.64	1.64	1.64	1.65
48	1.65	1.66	1.66	1.67	1.67	1.68	1.68	1.69	1.69	1.70
49	1.70	1.71	1.71	1.72	1.72	1.73	1.73	1.74	1.74	1.75

*The specific gravity of the dried slurry is assumed to be 2.65, and the slurry is assumed to contain no entrained air. Since the specific gravity of individual dried slurries may depart from 2.65, and entrained air is usually present in slurry in variable amounts, the factors in the table must be considered as approximate values and are therefore expressed only to two decimal places.

The table is based upon the equation,

$$\text{Factor} = \frac{k[100 + (d - 1)w]}{d(100 - w)}$$

in which d = specific gravity of dried slurry

w = per cent moisture

k = arbitrary constant

Assuming $d = 2.65$, and selecting 1.272 as a value of k which will make the factor for 30 per cent moisture slightly greater than 1.00, the equation reduces to the form,

$$\text{Factor} = \frac{48 + 0.792w}{100 - w}$$

Part IV — Direct Control of Potential Composition

THE FOREGOING STUDY of proportioning methods is concerned with the problem of controlling potential composition in processes in which there is no opportunity for calculating proportions of materials from complete analyses. Complete analyses are required in determining the carbonate requirement, but are not completed in time for direct application to specific problems. However, it has been shown that they can serve a useful purpose if changes in the carbonate requirement occur slowly.

When a complete analysis of each tank of slurry can be made before the slurry is released, combinations of slurries can be made in proportions calculated from the complete analyses. This constitutes direct control of potential composition.

desired potential C_3S , in this case assumed to be 60 per cent.

Deviations of the potential C_3S from the desired value, 60 per cent, are shown on the last line of the table. These values are converted to an unignited basis by multiplying by $(100 - \text{loss})/100$. For example, the ignition loss of slurry No. 1 is 38.21 per cent. The C_3S deviation on an unignited basis is 35.6×0.6179 , or 22.0 per cent.

Taken in reverse order, the C_3S deviations, on an unignited basis, represent relative weights of the slurries, dry basis, required for a mixture with the desired 60 per cent potential C_3S ; that is, 45.8 parts by weight of slurry No. 1 and 22.0 parts by weight of slurry No. 2, each on a dry weight basis, will form a mixture of the desired composition. These rela-

	Ignited basis		Unignited (dry) basis		Wet basis	
	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
Laboratory Determinations						
SiO ₂	19.14	26.54				
Al ₂ O ₃	5.66	7.39				
Fe ₂ O ₃	3.48	3.85				
CaO	69.78	60.38				
Carbonates*			78.9	72.6		
Ignition loss			38.21	35.56		
Moisture					32.3	37.1
Calculated Values						
Potential C_3S **	95.6	—11.1				
C_3S deviation	+35.6	—71.1	+22.0	—45.8		
*By rapid control method.						
**Calculated by equation 1.						

In discussing the indirect method, based upon determinations of the carbonate requirement at regular intervals, it was emphasized that it can be applied only when changes in the carbonate requirement occur slowly. The direct method is not subject to this condition. Since each combination of slurries is made on the basis of complete analyses, abrupt variations in the composition of the raw materials do not interfere with control of potential C_3S or C_2S . In addition, there is the possibility of controlling more than one constituent, as will be shown.

Control of One Constituent

The following data for two tanks of slurry, No. 1 and 2, will be used in illustrating methods of estimating proportions of slurries to obtain a

tive weights are used in estimating the relative volumes of slurry required and the carbonate content of the mixture, as will now be shown.

Slurry	Per cent Moisture	Factor (Table 3)	Rel. Wt.	Rel. Vol.
No. 1	32.3	1.09	45.8	49.9
No. 2	37.1	1.23	22.0	27.1

Relative volumes of slurry are obtained by multiplying each relative weight, dry basis, by a factor obtained from Table 3. The computations in this case are shown above.

From these relative volumes the number of feet of slurry in tanks of the same diameter can be calculated. For example, if 30 ft. of slurry No. 1 is used, the required quantity of slurry No. 2 is $30 \times 27.1/49.9$, or 16.3 ft.

The carbonate content of the mixture may be calculated as indicated below.

Slurry	Relative weights (unignited)		Carbonate Content		
No. 1	45.8	×	78.9	=	3614
No. 2	22.0	×	72.6	=	1597
Total	67.8				5211

$$\text{Carbonate content} = \frac{5211}{67.8} = 76.9\%$$

It is good practice to determine the carbonate content of the mixture, to test the accuracy with which the proportioning has been accomplished. In this case, the carbonate content should be 76.9 per cent. If the value obtained differs from this value to a greater extent than is considered allowable, an adjustment should be made. In deciding upon the degree of accuracy required in this adjustment it should be borne in mind that each 0.1 per cent deviation in the carbonate content is equivalent to a deviation of about 1.4 per cent in potential C₃S.

Graphic Method. The proportions of slurries, on a dry weight basis, required to obtain a desired potential C₃S or C₂S, and the carbonate content of the mixture, may be determined graphically. This is illustrated in Fig. 4 for the foregoing problem. The C₃S deviation, unignited basis, and the carbonate content of each slurry are plotted in the figure as indicated at the points designated as slurries No. 1 and 2. For example, the point for slurry No. 1 is located at 22.0 per cent C₃S deviation and 78.9 per cent carbonates. The line joining these points is divided into

two segments by the vertical line representing zero C₃S deviation. The lengths of these segments represent the relative weights of the two slurries, dry basis, required to obtain the desired potential C₃S. The segment farthest from the point for either slurry represents the relative weight of that slurry, as indicated in Fig. 4. In this figure only 10 per cent intervals for C₃S deviations and two per cent intervals for carbonate content are shown, but for accuracy in locating points and in measurements a sheet of graph paper is used. In the original graph from which the figure is drawn, the lengths of the segments are 10.1 and 4.85 in. These are the relative weights of slurries No. 1 and No. 2, respectively, on a dry basis.

The line joining the two slurries in Fig. 4 intersects the vertical zero C₃S deviation line at 76.9 per cent carbonates, which is the carbonate content of the mixture.

The relative weights of slurry, on a dry basis, are not identical with the proportions obtained by computation, but they are in the same ratio, which is all that is necessary. They may be converted to relative volumes by the method described previously.

Control of Two Constituents

In considering control of two constituents, it will be assumed that the constituents to be controlled are C₃S and C₃A. It should be understood, however, that the methods which will be described may be applied to any two constituents; for example, to C₂S and C₃A. Estimation of the proportions of slurries to obtain desired per-

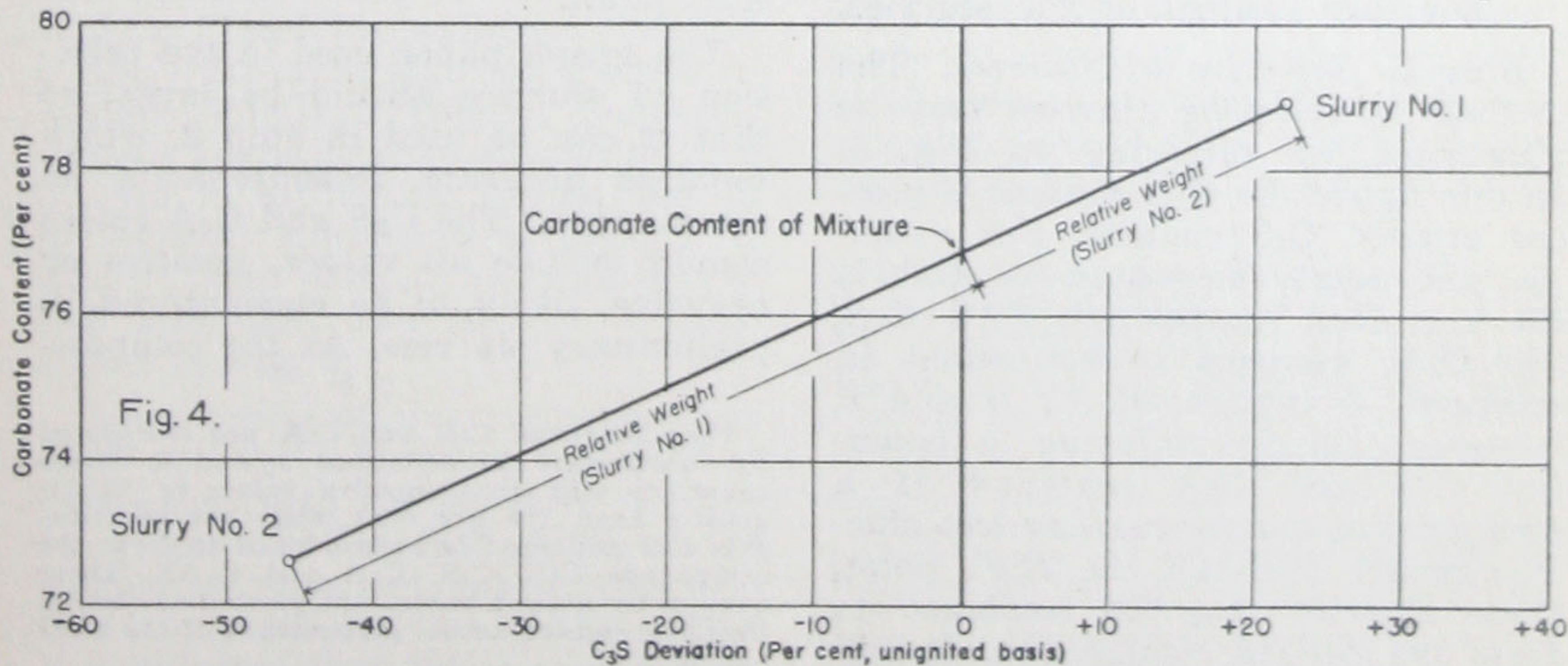


Fig. 4: Graphic method for control of one constituent

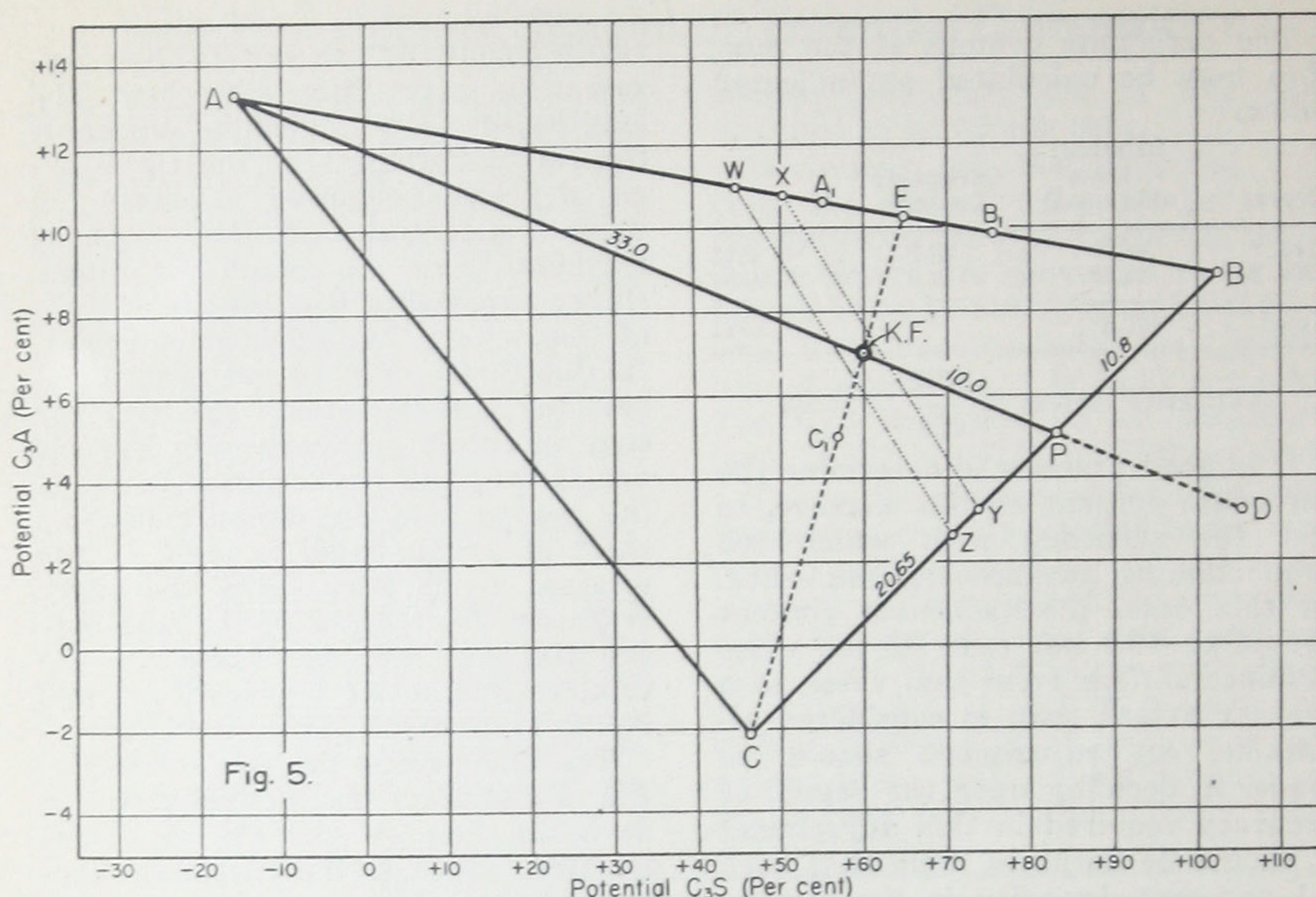


Fig. 5: Graphic method for control of two constituents

centages of C_3S and C_3A involves three successive steps:

1. The selection of slurries capable of forming the desired mixture. This is performed graphically.
2. Estimation of proportions of the slurries. Since C_3S and C_3A are expressed on an ignited basis, the proportions obtained in this step are on an ignited weight basis. Since graphic methods are particularly advantageous in two-component control, algebraic methods will not be discussed.
3. Conversion of proportions obtained in step 2 to proportions by volume, taking into account the moisture content of the slurries.

Step 1. Selection of Slurries. The method of selecting slurries may be illustrated by referring to Fig. 5. In this figure the C_3A content is plotted against C_3S content. For example, the point designated as *K.F.* is the kiln feed composition, 60% C_3S , 7% C_3A , assumed to be sought in mixtures. Points *A*, *B*, *C*, *D* and *P* represent slurries differing in potential C_3S and C_3A content† If a straight line connecting any two slurries passes through the *K.F.* point, these slurries may be combined to form the desired composition. It will

be seen then that the *K.F.* composition may be obtained by combining slurries *A* and *P*, *A* and *D*, or *C* and *E*.

Slurries which may be combined in pairs to form the *K.F.* composition will be encountered only occasionally. Usually three slurries are required. In that case the *K.F.* composition can be obtained from three slurries if the *K.F.* point is inside the triangle formed by joining the points representing the slurries. For example, slurries *A*, *B* and *C* may be combined to form the *K.F.* composition. On the other hand, slurries *B*, *C* and *D* can not be used, since a triangle joining these points would not include the *K.F.* point.

The graph paper used in the selection of slurries should be large, so that it can be used in step 2, which requires accurate measurements on the diagram. The C_3S and C_3A scales should include all values, positive or negative, likely to be encountered in preliminary slurries. As the composi-

†The potential C_3S and C_3A are calculated by substitution in equations 1 and 3. These equations will give negative values or values greater than 100 per cent when the constituents can not possibly be combined to form the compounds C_3S , C_2S , C_3A and C_4AF . These apparently absurd values are plotted as though they represented actual percentages of the compounds.

	Ignited basis			Unignited (dry) basis		
	Slurry A	Slurry B	Slurry C	Slurry A	Slurry B	Slurry C
Laboratory Determinations						
SiO ₂	26.86	18.66	19.80			
Al ₂ O ₃	7.47	5.55	5.95			
Fe ₂ O ₃	3.86	3.46	10.57			
CaO	59.99	70.40	61.87			
Carbonates*				72.1	80.4	73.3
Ignition loss				35.4	38.4	35.8
Potential Composition**						
C ₃ S	—15.7	102.5	46.3			
CA	13.27	8.86	—2.11			

*By rapid control method (acid-alkali or calcimeter).

**Calculated by equations 1-4.

SLURRY (WET) BASIS

Slurry	Per cent Moisture
A	35.3
B	41.9
C	39.7

tion of each slurry is reported, a point representing the slurry is entered in the diagram, to be erased when the slurry is no longer available. The diagram then also serves as a guide in the preparation of preliminary slurries, since slurry compositions suitable for combination with those already available can be seen at a glance. The preparation of preliminary slurries for two-component control will be considered in greater detail after presenting step 2.

Step 2. Estimation of Proportions (Graphic Method). The graphic method of estimating proportions of materials is an adaptation of a method which has long been in use for the estimation of phases in the interpretation of phase diagrams. The application of this method to the proportioning of cement raw materials was described in 1927 by E. S., W. S., and W. A. Ernst, and in 1929 by R. Grun and G. Kunze.* It was first applied in routine raw mix control by R. M. Willson** and his assistant chemists at the Victorville plant of the Southwestern Portland Cement Company. In their operations the graphic method is used in estimating proportions of preliminary slurries, to secure a final slurry with desired percentages of C₃S and C₃A. The method is illustrated in Fig. 5.

The plotting of slurry compositions (C₃S and C₃A) has been described in connection with the selection of slurries (step 1). The *K.F.* point can be located to represent any desired kiln feed composition, but in this figure it is assumed that 60% C₃S, 7% C₃A,

is the composition sought. Points A, B and C represent the three slurries in the above table.

All of the compositions which can be made from two slurries are on the straight line joining the slurries. For example, slurry *P*, Fig. 5, can be made from slurries *B* and *C*. The lengths of the lines *CP* and *BP* are the relative proportions of *B* and *C*, respectively, required to form slurry *P*. The lengths of these lines in the original diagram on a larger scale are indicated in the figure. It is seen that 20.65 parts by weight of slurry *B* may be combined with 10.8 parts by weight of slurry *C*, to form 20.65 + 10.8, or 31.45 parts by weight of slurry *P*.† Since the diagram is based upon C₃S and C₃A percentages on an ignited basis, these values are on *ignited weight* basis.

Following the same procedure, it is found that the relative proportions of slurries *A* and *P* to form the *K. F.* composition are 10.0 and 33.0, respectively. If slurry *A* is to be used with 31.45 parts by weight of slurry *P* (the quantity formed from slurries *B* and *C*), $10 \times 31.45/3.0$, or 9.53 parts by

*Proportioning Raw Materials. Edgar S. Ernst, Walter S. Ernst and Wm. A. Ernst. *Rock Products*, Oct. 15, 1927, pp. 73-76.

A Graphic Method of Proportioning the Raw Mix. Dr. Richard Grun and Dr. Gunther Kunze. *Concrete, Cement Mill Section*, Jan., 1929, pp. 115-124.

**Chief Chemist, Southwestern Portland Cement Co., Victorville, Calif.

†Since the slurry nearer to the desired composition is used in the greater quantity, the length of the line farther from *B* is the relative proportion of *B*, and the length farther from *C* is the relative proportion of *C*. This principle is followed in every case.

weight will be required. Thus we have the relative proportions of slurries A, B and C, as follows:

Slurry	Relative proportions (ignited weight basis)
A	9.53
B	20.65
C	10.8

In obtaining the relative proportions on an ignited weight basis, a line was drawn from vertex A through the K. F. point to P. Any vertex could have been selected for the purpose. For example, a line from vertex C through the K. F. point to E might be drawn, as indicated by the broken line in the figure, and the same procedure followed in estimating relative proportions of slurries A, B, and C. The values obtained will not be the same as those found above, but they will be in the same ratio to one another, which is all that is necessary.

Relative proportions on an ignited basis are converted to relative proportions on an unignited basis by dividing each value by (100 — ignition loss)/100, indicated in table below.

Slurry	Ignition loss	Rel. proportions (ignited basis)		$\frac{100 - \text{loss}}{100}$		Relative proportions (unignited basis)
A	35.4	9.53	÷	0.646	=	14.75
B	38.4	20.65	÷	0.616	=	33.52
C	35.8	10.8	÷	0.642	=	16.82

In the footnote to Table 3 attention is called to the fact that the factors for conversion to a volume basis are only approximate. In addition, further errors may be introduced because of the lack of precision in volume measurement of slurry in the plant. If the three slurries to be combined are all close to the desired mix composition, errors from these causes are not likely to be significant, and the calculated relative volumes can be used without further tests. In this case, slurries A, B, and C are not close to the desired K. F. composition,

and it is necessary to check the proportioning operation by tests for carbonate content. In addition, since this method of checking is valid only for combinations of two slurries, it will be necessary to combine two of the three slurries, testing this mixture for carbonate content and adjusting proportions, if necessary, before adding the third slurry; that is, the operation is carried out in two stages, each involving the combination of two slurries.

The relative proportions on an unignited basis are converted to relative proportions on a slurry volume basis by applying the factors for moisture content from Table 3, as shown at the bottom of this page.

Before proceeding with a description of the use of carbonate determinations in obtaining correct proportions on a dry weight basis, it should be emphasized that the carbonate determinations do not serve the purpose when three slurries are combined before testing. This is true for two

reasons, as follows.

1. The mixture may be far from the desired composition, and yet meet the requirements as to carbonate content. For example all mixtures in the area WXYZ, Fig. 5, are within 0.2 per cent of the carbonate content of the K. F. composition. This includes a wide range of percentages of C₃S and C₃A.
2. If the carbonate content is too far from the K. F. composition to be considered satisfactory, the correction to be applied is not known. For example, the C₃S and C₃A content of a mixture too high in carbonate is not known. It may be corrected for carbonate content by the addition of either slurry A or B (Fig. 5). The fact that the carbonate content is high provides no information as to which slurry will bring it closer to the K. F. composition. The wrong choice may even bring it farther from the desired composition.

Slurry	Per cent moisture	Factor (Table 3)		Relative proportions (unignited basis)		Rel. proportions by volume
A	35.3	1.17	×	14.75	=	17.3
B	41.9	1.40	×	33.52	=	46.9
C	39.7	1.32	×	16.82	=	22.2

As will be shown presently, there is sometimes a reason for choosing a particular pair of slurries to be mixed first, before adding a third. In the case of slurries A, B, and C there is

MIXTURE OF SLURRIES A AND B

Slurry	Rel. proportions (unignited basis)	Carbonate Content
A	14.75	$\times 72.1 = 1063$
B	33.52	$\times 80.4 = 2695$
Total	48.27	3758

$$\frac{3758}{48.27} = 77.9 \text{ per cent carbonates}$$

MIXTURE OF SLURRIES A, B, and C

Slurry	Rel. proportions (unignited basis)	Carbonate Content
A	14.75	$\times 72.1 = 1063$
B	33.52	$\times 80.4 = 2695$
C	16.82	$\times 73.3 = 1233$
Total	65.09	4991

$$\frac{4991}{65.09} = 76.7 \text{ per cent carbonates}$$

no particular choice. We may select any pair, and will select slurries A and B arbitrarily. It will be necessary, then, to determine the carbonate content to be sought when combining slurry A and B, and when combining this mixture with slurry C. These values are found as indicated above.

It was found previously that slurries A, B, and C are to be used in the proportions 17.3, 46.9 and 22.2 parts by volume, respectively. The procedure is to combine slurries A and B in the proportions indicated, then determine carbonate content. If the carbonate content departs from 77.9 per cent to a greater extent than is considered satisfactory, an adjustment in proportions is made. Slurry C is then added to the mixture, and the carbonate content determined. If it departs too much from 76.7 per cent, an adjustment should be made. Because the mixture of slurries A and B already has been adjusted and the

entire quantity is used in making the final mixture, an excess of slurry C should be avoided. In deciding upon limits to be assigned to the carbonate content, it should be borne in mind that a deviation of 0.1 per cent in carbonate content is equivalent to about 1.4 per cent deviation in C_3S . By this procedure, with reasonably small limits on carbonate content in each stage, the potential C_3S and C_3A values sought can be obtained with a satisfactory degree of accuracy, even though the slurries to be combined depart considerably from the desired composition.

The Preparation of Preliminary Slurries. In the procedure which has been described, the time consumed in obtaining the desired composition in each stage depends upon the chances of obtaining the calculated carbonate content, within assigned limits, when proportioning by volume. If the carbonate content is correct in most cases, little time is consumed in making adjustments and in testing the mixtures after adjustment. On the other hand, a great deal of time may be consumed in these operations if adjustments are usually required. On that account, some consideration should be given to methods of avoiding frequent adjustments of proportions. When such adjustments are required too frequently, there is likely to be a tendency to widen the limits on carbonate content which will be accepted as satisfactory. This will reduce the frequency of adjustments, but it is not a real solution, since it means the acceptance of a wider range of percentages of potential C_3S and C_3A in the final mixture. For example, if a carbonate content within 0.7 per cent of the calculated carbonate content is accepted as satisfactory, it is equivalent to accepting a range of about 14.0×0.7 , or 10 per cent, on each side of the C_3S content sought. The limits on carbonate content should be assigned with reference to the range of values of C_3S which is considered acceptable. If adjustments are required too frequently, other means of avoiding them should be employed. These are concerned with the preparation of preliminary slurries which are combined to form the final mix.

Steps which can be taken to simplify the operations in control of two constituents may be illustrated by reference to Fig. 5. As mentioned previously, slurries *A* and *B* are mixtures of limestone and shale, while slurry *C* is a mixture of the same raw materials, but with high-iron material added to reduce the potential C_3A content. Let us suppose that the limestone-shale mixtures are prepared more accurately than *A* and *B*, so that slurries A_1 and B_1 are obtained instead. Less high-iron material may be used in preparing the third slurry, obtaining a composition such as C_1 instead of *C*. Since slurries A_1 , B_1 , and C_1 are close to the *K. F.* composition, the proportioning operation does not need to be carried out as accurately as in the case of slurries *A*, *B*, and *C*. The three slurries can be mixed simultaneously in the calculated proportions by volume, and no test of carbonate content should be required.

The combination of slurries *A*, *B*, and *C* and the combination of slurries A_1 , B_1 , and C_1 represent two extremes. Accurate proportioning of *A*, *B*, and *C* requires two stages, each subject to check by carbonate determinations, with the necessity of frequent adjustment of proportions. Slurries A_1 , B_1 , and C_1 may be combined in one operation, without such tests and adjustments. The latter condition may not be attainable with the equipment available in the plant, but an approach to it will simplify operations in seeking reasonably accurate control of two constituents. Anything which can be done to bring preliminary mixtures closer to the desired composition will reduce the frequency with which adjustments of proportions are required, even if the need for checking by carbonate determinations is not eliminated.

There are some instances in which the second stage of the proportioning operation can be simplified by a proper choice of slurries to be combined in the first stage. For example, let us suppose that slurries *A*, *B*, and C_1 are to be combined to form the *K. F.* composition. Since C_1 and *E* are close to the *K. F.* composition, slurry *E* may be made by combining *A* and *B*, with

tests for carbonates and adjustment of proportions. Slurries C_1 and *E* may then be combined in calculated proportions by volume, without the need for carbonate tests. If slurries *A* and C_1 , or *B* and C_1 , are combined in the first stage, conditions are not as favorable for proportioning by volume, and carbonate determinations are required in both stages, with the possibility of a need for adjustment of proportions in either stage.

In the case just described, slurry C_1 is used in greater proportion than slurries *A* and *B*. At some plants it may be convenient to prepare a high-iron slurry with such a high percentage of Fe_2O_3 (low or negative C_3A) that it will be used in small proportions in each combination. The percentage of Fe_2O_3 may be much greater than in slurry *C*, but the procedure may be described with reference to slurry *C*. Let us assume that the limestone and shale, or equivalent materials, are proportioned with a fair degree of accuracy, so that slurries A_1 and B_1 are obtained. Slurries A_1 and B_1 may be combined first to form slurry *E*, without carbonate tests, and slurry *C* may then be added, and carbonate tests applied to insure accuracy. On the other hand, if slurries A_1 and *C*, or B_1 and *C*, are combined first, carbonate tests are required in the first stage. In the second stage they may be found necessary, but the chances are favorable for obtaining the desired carbonate content, with few occasions in which adjustment of proportions is needed. Here there is a choice between simplifying the first or second stage. In general, simplification of the second stage is preferable, since the total quantity of slurry made in the first stage is used in the second stage. An adjustment requiring an additional quantity of this slurry introduces an awkward situation which can be avoided, at least most of the time, by simplifying the second stage.

APPENDIX B

Derivation of Equation for Effect of an Added Material on the Carbonate Requirement

Equation 7 in the text refers to the effect of the addition of iron ore or sand to the raw mix on the carbonate requirement. The equation has a more general significance, however. It refers to the addition of any material, composed of one or more of the major components of portland cement clinker. For example, the equation may be applied to materials used as a source of alumina, to a clay or shale not originally present in the mix, etc. Because the equation does not refer only to the addition of iron ore or sand, reference to these particular materials will be avoided here, and the added material will be referred to as an "additive."

The symbols used in the derivation are shown at the bottom of this page.

It should be noted that A is the potential C_3S (or C_2S) to be maintained in the mix, both before and after the introduction of the additive. The quantity p is the carbonate content of a correctly proportioned mix before the introduction of the additive, that is, p is the carbonate requirement. The carbonate content is increased by the amount x when the additive and limestone are introduced, as indicated in the last column. It is the quantity x which is sought. The quantity S is 100 minus the ignition loss in the correctly proportioned mix. The value of S need not be known, since S drops out in the course of the derivation. The sum of the fractional weights of the materials is always unity. The fractional weight of the original mix is therefore $(1 - r - s)$.

The percentage of any constituent in the final mix is the sum of the products obtained by multiplying the percentage of that constituent in a material by the weight fraction of the material. Since carbonates are expressed on an unignited basis, the weight fractions on an unignited basis are used in setting up the equation for carbonates. For a similar reason, the weight fractions on an ignited basis are used for C_3S . The equations obtained in this manner are shown below.

Carbonates:

$$P(1 - r - s) + p_1r + p_2s = p + x \quad (1)$$

C_3S :

$$\frac{AS(1 - r - s) + A_1S_1r + A_2S_2s}{S + (S_1 - S)r + (S_2 - S)s} = A \quad (2)$$

Collecting terms in equation 1,

$$(p_1 - p)r + (p_2 - p)s = x \quad (3)$$

Upon simplifying equation 2, S drops out, leaving the equation,

$$S_1(A_1 - A)r + S_2(A_2 - A)s = 0 \quad (4)$$

Eliminating s from equations 3 and 4,

$$x = r \left[p_1 - p + \frac{S_1(p_2 - p)(A - A_1)}{S_2(A_2 - A)} \right]$$

Let F represent the increase in carbonate requirement due to the introduction of 1.0 per cent of the additive. Then $r = 0.01$, and

$$F = \frac{1}{100} \left[p_1 - p + \frac{S_1(p_2 - p)(A - A_1)}{S_2(A_2 - A)} \right]$$

which is equation 7 in the text.

APPENDIX A

Preparation of Raw Mix Sample for Analysis

The first step in the complete analysis of a raw mix sample is to render it acid-soluble by fusing it with sodium carbonate or by heating it to a temperature high enough to form a clinker. Fusion with sodium carbonate introduces large amounts of sodium salts into the solution. As a result, the time required for analysis is increased, because double precipitation is required to secure satisfactory accuracy. On that account it is recommended that the sample be prepared for analysis by heating at a temperature high enough to convert it to clinker.

Burners and muffle furnaces commonly used for ignitions and fusions in analytical work do not develop the temperatures required for clinkering raw mix samples. In some laboratories the raw mix samples are clinkered in an electric arc, forming a button more dense than a normal clinker, to be ground for analysis. A high temperature furnace of the "global" type, in which the heating elements are rods of carborundum, is used in other laboratories.

The global type furnace is convenient in some respects, but has the disadvantage that it must be kept in continuous operation. Repeated cooling below a dull red heat causes the heating elements to deteriorate rapidly. A crucible furnace utilizing gas and compressed air has the advantage that the cold furnace can be brought up to temperature very rapidly, producing a satisfactory clinker in 15 minutes after a cold start. The writer has had no experience with a gas-fired crucible furnace, but our attention has been called to the fact that a crucible furnace supplied by the Selas Company has proved satisfactory.

The time and temperature required for obtaining a satisfactory clinker for analysis will depend upon the composition of the sample. It is advisable to determine the lime or carbonate content before clinkering the sample. Samples low in carbonates require a lower temperature, or less time, than samples high in carbonates. Since other components of the mix also have an influence, the procedure to be followed must be learned by experience with the materials in use at the plant.

	Raw Mix before addition	Additive	Limestone to balance additive	Final mix after addition
Weight fractions of materials (unignited weight basis)				
	$1 - r - s$	r	s	
Percentages of constituents				
C_3S (or C_2S)	A	A_1	A_2	A
Carbonates	p	p_1	p_2	$p + x$
100-ignition loss	S	S_1	S_2	
Weight fractions of materials (ignited weight basis)*				
	$\frac{S(1 - r - s)}{D}$	$\frac{S_1r}{D}$	$\frac{S_2s}{D}$	

$$*D = S(1 - r - s) + S_1r + S_2s = S + (S_1 - S)r + (S_2 - S)s$$

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